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

Annual Report for Period
October 1, 1988 to September 30, 1989
Issued May 1990
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Prepared for:
National Institute of Dental Research
Bethesda, MD 20892

U.S. DEPARTMENT OF COMMERCE
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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 used as well as 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 with laboratory test data. 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 89 SIGNIFICANT ACCOMPLISHMENTS

- A series of polymer-modified glass-ionomer cements were prepared as a means of forming toughened, mechanically strong dental cements. The polymer-modified cements showed enhanced bonding to composites in comparison with the unmodified glass-ionomer cements.

- A series of new polymeric calcium phosphate cements were developed based on the setting reaction of tetra calcium phosphate and dicalcium phosphate in aqueous solutions of polymers. In some of the polymer solutions significant conversion to hydroxyapatite occurred.

- Certain organozirconates were shown to improve the interfacial bonding of glass fillers in dental composites.

- Organometallic methacrylate monomers were synthesized which show promise for use as radiopacifing resins in dental applications. The mechanical strengths of some composites formulated with organometallic resins were comparable to BIS-GMA type resins.

- A liquid carboxylic acid-containing monomer was synthesized and, by Weibull analysis, tested favorably in the new Bowen adhesion procedure for bonding composites to dentin.

- A new technique for determining the water content and solubility of resin based dental materials using near infrared spectroscopy (NIR) was developed.

- A saturated liquid spiro orthocarbonate monomer was prepared to investigate alternate means of achieving double ring-opening polymerization with expansion in volume.

- Monomers capable of efficient cyclopolymerization were found to have low polymerization shrinkage values. The influence of various ester functionality on synthesis and polymerization of these monomers was evaluated.

- Mutifunctional reactive oligomers based on the cyclopolymerizable substructure were prepared and used in place of BIS-GMA to provide tougher composites.

- The method used to prepare the cyclopolymerizable monomers was applied to yield highly fluorinated difunctional monomers from readily available monofunctional fluoroacrylates.

- The polymerization shrinkage dialatometer was modified and rendered more stable; the system reaches stability after reactions, within five minutes, to the level of baseline uncertainty and remains stable up to 24 hours.

- A patent was applied for on the use of microwave generated gas plasmas for sterilization of dental instruments. One American company entered into a cooperative research and development agreement for developing the technology for commercialization.

- An algorithm was developed for analysis of clinical data according to a censored Weibull distribution with nonuniform insertion times and failures plus removals from the study. The analysis allows prediction of characteristic lifetimes and time to failure at any specified failure level.

- A conference was held at NIST entitled "Modern Instrumentation and Analysis Techniques" Co-sponsored with the Academy of Dental Materials.

- An analysis of the diametral-compression test revealed that only single cleft fractures can be used for diametral tensile strengths (specimen failure into two halves along the diametral plane). Comparisons of loads to failure require failures of the same mode, either single, double or triple cleft. Different failure modes cannot be mixed.

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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) metrology, diagnostics and related topics. 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 such as investment variations. 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. Weibull statistics is employed for analyses of the strengths of dental systems, time to failure etc. A special effort has also been mounted to explore the use of plasma's for sterilization of dental instruments. (Measurements of spore populations etc. will be conducted with cooperation of the U.S. Navy).

I. COMPOSITES, CEMENTS AND ADHESION

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

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 poor mechanical properties, high solubility and lack of resistance to wear and disintegration deter their more extensive use, especially for cementation for permanent prostheses or for their use as intermediate restoratives.

Non-eugenol containing cements based on vanillate esters, o-ethoxybenzoic acid (EBA), and zinc oxide, have been developed in this laboratory [1-7][1]. 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, and (5) adhere strongly, even on prolonged water exposure, to non-precious metals, porcelain and composites. The cements greatly exceed requirements of ANSI/ADA Specification No. 30 for Type 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 methacryloxyethyl 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

---

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

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) furnish assistance and guidance to conduct investigations of the biocompatibility and toxicity of the cement and its ingredients and 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 and in the previous reports. These investigations have led 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, and (3) complete 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 this phase during the year.

Phase II. New Applications of These Materials

No studies were conducted on phase II during the year due to emphasis on other portions of the research. One review stressing the commercial suitability of these cements for diverse applications has been prepared for publication. Another review summarizing the properties of these cements and intermediate restoratives has been published [18].

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

(1) Biocompatibility

Past Accomplishments

Vanillate and syringate cements prepared in this laboratory have been subjected to the biological tests suggested in the

ANSI/ADA specification No. 41. They pass all these tests. Their pulp irritation is similar to ZOE cements. Summaries of these studies are given in the previous annual reports and references 9-14 and 16-17. These cements have been made available to interested parties for selected clinical studies.

Progress

(a) Biological Evaluation of Zinc Hexyl Vanillate Cements

The cellular and tissue response studies to hexyl vanillate (HV), ZOE and zinc phosphate (ZP) cements were continued by Dr. J. C. Keller and coworkers at the Medical University of South Carolina. The cellular and connective tissue reactions to HV approximated those of ZOE and ZP cements and demonstrated the acceptable biological performance of HV cement. The results have been written up. The manuscript has been accepted for publication in "Dental Materials".

(b) Biological Evaluation of Vanillate Intermediate Restoratives.

Studies at the University of Texas at San Antonio and University of Tennessee are continuing to determine the biological characteristics of formulations synthesized in this laboratory containing dicyclopentenyloxyethyl methacrylate or cyclohexyl methacrylate and silanized glass which have much improved properties compared to commercial intermediate restoratives.

(c) Assistance in Clinical Evaluation

The use of these cements in clinical studies is encouraged. Materials have been synthesized for Dr. Baez at the Dental School, University of Texas at San Antonio, who subject to funding, is interested in such a project. A clinical study of the usefulness of these cements as restorative bases is being outlined by Dr. Parker of the Navy Dental School (Bethesda, MD).

The vanillate cement have been used in a limited clinical study at the Louisiana School of Dentistry. No adverse effects were noticed in their use.

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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 in 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 the composites are responsible for color instability. Such data should assist in the development of more color stable resins.

Accomplishments

The color stability of composites on exposure to irradiation by (1) 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 investigated. Composites studied included chemically and light cured hybrid and microfilled resins, and a material copolymerized by light and chemical aftercure. Analytical high pressure liquid chromatography identified the major constituents of composite pastes. Color changes of composites intensified on increasing the irradiation time. Exposure to the light sources under similar conditions gave comparable results. Visible light cured materials were more color stable than two common chemically cured composites. Light shades yielded more visible color changes than dark shades of the same brand. There was a significantly more severe discoloration of composites kept in water at 60°C than for those stored in air. Comparison with results in two clinical studies of color changes using two of the chemically cured composites investigated here, indicates that these restoratives, which pass the ANSI/ADA and the ISO specification tests, discolor in clinical use after 2-3 years. Because of the intense discoloration which had occurred, quantitative estimation of the color changes which took place after one year water storage proved difficult.

PROGRESS REPORT

Phase I. Characterize Minor Components of the Composites. Correlate Aging Behavior with Presence of Specific Ingredients

Characterization of the minor components awaits access to a preparative chromatograph. Such an instrument will allow separation of quantities of these constituents sufficient for identification by analytical techniques such as infrared or NMR.

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.

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C. Development of Radiopaque Copolymeric Denture Resins

Overview

The ever increasing use of plastics in dentistry makes it desirable and often mandatory that the 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 acrylate, bismuth subnitrate or yttrium fluoride as fillers [5-8], or (3) incorporation of an element of 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]. Permanent radiopacity can also be achieved by entrapping polymer salt complexes such as those prepared on chelating copolymers of methyl methacrylate with $BaBr_2$ to produce polymer salt complexes in an interpenetrating poly (methyl methacrylate) network [15,16]. 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. 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 presence of aromatic monomers in the polymerizable paste greatly reduces the storage stability of such mixtures.

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.

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.

Monomers with a high percentage of atoms of high molecular weight such as pentabromophenyl or triiodophenyl methacrylate are compatible with methyl methacrylate [17]. The pentabromophenyl methacrylate (PBPMA) is commercially available and the triiodo derivative (TIPMA) 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 [17].

Objective

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

Accomplishments

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 the deficiencies suspension polymer made up from 10% pentabromophenyl methacrylate and 90% methyl methacrylate was synthesized employing a commercial procedure. Using a dough prepared from methyl methacrylate monomer and the suspension polymer powder, cured denture base specimens with different powder-liquid ratios were evaluated. The radiopacity of the cured materials was excellent. The physical properties such as translucency, water sorption and color stability of the material were good. The commercial methyl methacrylate liquid employed in this formulation passed the thermal stability specification for denture base polymers. To improve the mixing characteristics, additional quantities of pentabromophenyl methacrylate have been synthesized. Difficulties were encountered in preparing powder particles of the proper particle size and with a minimum degree of crosslinking. Such powders are necessary to obtain mixes with desirable working characteristics and short doughing and setting times. To prepare compositions with optimal clinical desirable properties, detailed studies of the effect of plasticizer and comonomers to increase swelling behavior of the powder will have to be conducted.

PROGRESS REPORT

Phase I. Using Commonly Accepted Testing Procedures, Study the Curing Characteristics and the Physical, Chemical, Esthetic and the Radiopaque Properties of Self-Curing Denture Base Materials

Prepared from Copolymers of Pentabromophenyl- and Triiodophenyl Methacrylate and Methyl Methacrylate Copolymers.

If we are successful in synthesizing non-crosslinked powders, the properties of denture base materials prepared from them will be evaluated.

Phase II. If the Properties of Formulation Studied in Phase I Pass all Requirements of the ANSI/ADA Specification for Denture Base Resins, Have Adequate Working Properties and Good Esthetic Characteristics, We Will 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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E. Monomers that Polymerize with Expansion

Introduction

Much effort has been directed at studying the effects of and reducing the magnitude of the shrinkage that accompanies the curing of dental composite resins. While advances have been made, the polymerization contraction exhibited by the current generation of materials is still sufficiently large to make the bonding of composites to a dentin substrate an unreliable process [1,2]. In bonding to acid etched enamel, where excellent adhesion and marginal integrity can be achieved, significant stresses are developed within the composite [3] which may limit the performance of the material.

One approach to minimize the polymerization shrinkage of composites has been the use of monomer ingredients which are capable of expansion during polymerization. The free radical polymerization of unsaturated spiro orthocarbonate monomers has been shown to occur by a double ring-opening process which results in a volume expansion [4,5]. In early investigation of one of these spiro monomers in dental resins [6], reduced polymerization shrinkage and improved adhesion to enamel were obtained. Our recent work involving this same class of spiro orthocarbonates for use in composites has led to new monomers which are more easily incorporated into dental resins [7]. In addition, new monomers have been devised which have reactivities that are more comparable with those of conventional acrylic monomers.

Objective

This project represents an attempt to minimize, if not completely eliminate, the stress-inducing polymerization shrinkage in dental adhesive and composite resin materials through the synthesis and utilization of novel spiro orthocarbonate monomers which expand upon polymerization.

PROGRESS REPORT

Phase I. Synthesis

New synthetic work carried out during this reporting period involved a departure from the vinyl-substituted, asymmetric spiro orthocarbonate compounds previously prepared in this study. A saturated, symmetrical spiro monomer 1 was obtained in good yield from a simple two-step synthesis. This compound, which is a liquid at room temperature, is suitable for cationic double ring-opening polymerization rather than the free radical process. Efficient cationic polymerization of spiro monomers with an expansion in volume has been reported [8-10]. In an attempt to find other modes of polymerization that will yield double ring-opened polymers, this type of monomer could be improved by increasing the asymmetry of the structure or by adding a flexible unit, the synthesis would be relatively difficult and will not be pursued currently at this time.

Phase IV. Evaluate the Properties of Polymers Formulated in Phase III.

The results of the diametral tensile strength (DTS) tests on the experimental composite materials is shown in Table I. These results indicate there is no significant decrease in mechanical strength associated with the use of spiro monomer 2 in the composites. The mechanical properties are maintained even though 2 is used in relatively large proportions and is known to be very inefficient at crosslinking during polymerization. These results represent an improvement over the approximate 20% decline in DTS values that was characteristic of formulations incorporating other less reactive spiro monomers [7]. As noted previously for other spiro orthocarbonate monomers utilized in dental composite formulations, the properties of the chemically cured experimental composites reported here were significantly better than those of the corresponding photo-cured materials. The polymerization shrinkage of the composite resin employing monomer 2 as a diluent is empirically less than that of the control formulation, however, this observation is currently being verified by specific gravity determinations.

Table I.

DTS of Chemically Cured Composites

Formulation (wt ratio)			DTS, MPa
Control A	EBPADM/HMGDM	(89.1:9.9)	42.1 ± 1.5
Exp. A	EBPADM/2/HMGDM	(67.6:24.6:7.5)	41.0 ± 2.4
Control B	BIS-GMA/TEGDMA	(70:30)	50.5 ± 1.3
Exp. B	BIS-GMA/2	(76.4:23.6)	48.6 ± 2.5

Phase V. Evaluation of Biocompatibility of Formulations Selected from Phase IV.

This work awaits completion of Phase IV.

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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 polymers). The synthesis of BIS-GMA 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 radiopaque glasses, quartz, minerals, ceramics, organic and hybrid organic-inorganic powders of various sizes, size distributions and shapes 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). Similar resin-based materials also are widely used in other applications (e.g., adhesives,core build-up and crown and bridge materials, laminating veneers, 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 polyelectrolyte cements (e.g., glass ionomer) and mineralized tissue also may explain their adhesion to tooth structure [4]. Other mechanisms for bonding to tooth structure will be discussed in Part IV, pp. 56-57 [5-16].

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) 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 polar compounds (e.g., acetic acid) are needed to activate the acid-base reactions and to achieve clinically acceptable setting times for (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. Development of Improved Interfacial Bonding Systems and Fillers for Composites and Cements. (Filler Portion of Project is New)
(Synthesis, Formulation and Evaluation)
IV. Bonding of New Resin Systems to Tooth Structure.
(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 and 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 filler phases 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 [24-26]. 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 of significant fluorocarbon or siloxane content 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 and/or chain transfer agents as well as other types of network forming agents that can augment the degree of cure and crosslink density [27-35]. Emphasis also is directed to monomers that have maximal cure and minimal polymerization shrinkage [35]. An ancillary part of this approach involves the development of more efficient, color stable initiator systems for ambient polymerizations of dental resins in a more uniform fashion [27,28,35].

PROGRESS REPORT

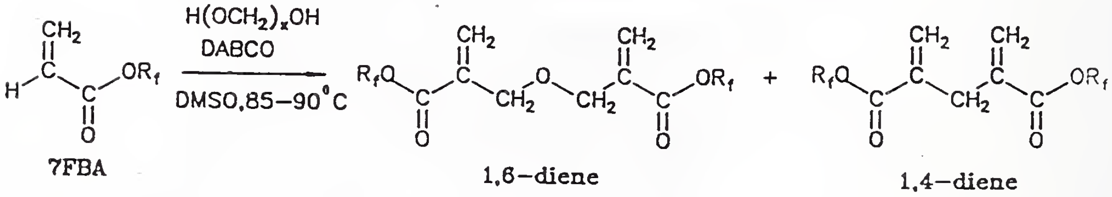
Phase I. Synthesis and Formulations

(a) New syntheses of multifunctional monomers of high fluorine content (partly new).

Highly fluorinated acrylic polymers, as is the case with other fluorocarbon polymers, have a number of unique properties, e.g. excellent solvent and chemical resistance, low water uptake, high lubricity, etc. Most fluoroacrylic polymers are derived from monofunctional monomers, which in turn are prepared usually by the esterification of the corresponding fluoroalcohol. Because of the lack of conveniently available fluorochemical intermediates (e.g. diols and polyols), comparatively few multifunctional fluoroacrylic monomers have been synthesized. This has been an ongoing problem in our efforts to develop suitable hydrophobic dental sealants and composites based on fluoro monomer systems.

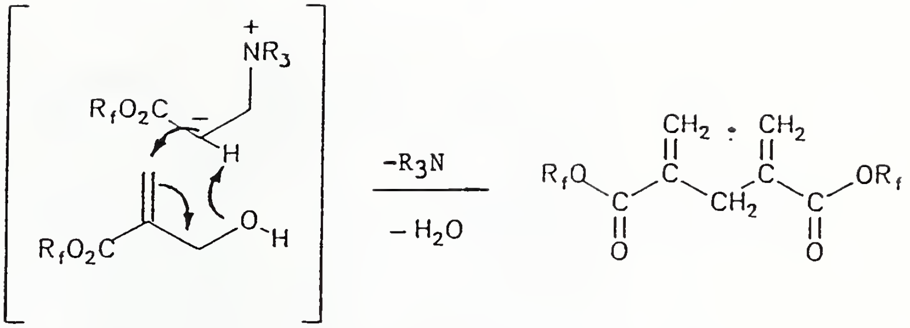
Recent research in this and other laboratories has shown that hydrocarbon alkyl acrylates (e.g. methyl acrylate) and diacrylates react with paraformaldehyde under ambient conditions in the presence of 1,4-diazabicylo[2,2,2]octane (DABCO) to form dimethacrylate ethers and oligomeric methacrylate ethers [36,37] (see f below). These unique monomers are highly reactive and because of this fact and the favorable steric arrangement of the vinyl groups, exhibit a propensity for inter-intramolecular cyclopolymerizations. This type of polymerization proceeds at ambient temperatures to yield polymers containing 6-membered rings in the backbone, low residual vinyl unsaturation, and reduced polymerization shrinkage [37].

In view of the relative ease of conducting this reaction and the availability of a number of monofunctional fluoroacrylates, we decided to explore the feasibility of extending this formaldehyde insertion reaction to the synthesis of difunctional and multifunctional fluorinated monomers that otherwise would not be readily available. The commercially available monofunctional fluoroacrylate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate (7FBA) was used in this preliminary study. The neat reaction of 7FBA with paraformaldehyde under ambient conditions with catalytic amounts of DABCO yielded even after long reaction times (1-5 month) only trace amounts of products (detectable by ^{1}HNMR). Major products included the expected 1,6-diene ether 1, an unexpected 1,4-diene (non-ether type) and an unidentified third olefinic product. The ratio of 1,4-diene to 1,6-diene was about 2. The structure of these products is shown below.



$R_f = CH_2CF_2CF_2CF_3$

A second experiment involved heating the reaction mixture for 30 hours at 85-90°C. Contrary to results found with alkyl acrylate reaction mixtures, no products were detected. A variation of the above reaction involved the addition of small amounts of dimethyl sulfoxide to the above mixture and the same heating regimen. After one hour at 85-90°C the mixture became homogeneous. After 30 hours, a major improvement in product yield was noted (^{1}HNMR), namely (~40%) 1,4-diene, (~20%) 1,6-diene, 20% of a 1,8 diene and small amounts of an unknown olefinic product. A possible mechanism for the formation of the unexpected 1,4 diene is depicted as follows:



We also have prepared the hexafluoro diacrylate 2,2,3,3,4,4-pentane-1,5-diacrylate, from the corresponding hexafluoropentane-1,5-diol. This diacrylate also reacted with paraformaldehyde/DABCO at elevated temperatures in DMSO. As expected oligomeric products are formed by chain extension reactions. These interesting reactions are the subject of further study and should yield monomers which can polymerize and crosslink to provide materials with high degrees of conversion and excellent resistance to chemical softening.

(b) Formulation and evaluation of dual-cured composites.

No work was done in FY89.

(c) Synthesis of highly fluorinated multifunctional methacrylates based on hexachlorocyclophosphazene has been dropped due to similar work being done elsewhere [33,34].

(d) Silyl ether derivatives

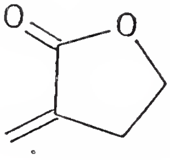
No work was done on this project in FY89.

(e) Synthesis of hydrophobic urethane derivatives of BIS-GMA.

No work was done on this project in FY89.

(f) Monomers and/or other additives to improve the physical and chemical performance of resin-based materials by increasing the degree of polymerization and crosslink density.

In a prior investigation, the incorporation of α-methylene butyrolactone I in small proportions to a BIS-GMA-triethylene glycol dimethacrylate control formulation provided an improved degree of conversion and an increase in mechanical strength properties [38]. The synthesis of high molecular weight methylene lactones was undertaken to reduce the magnitude of the shrinkage associated with the high conversion polymerization of these very reactive monomers. To achieve this benzaldehyde and cyclohexanone were converted to the corresponding methylene lactone derivatives II and III, respectively, in a one step reaction. The polymerization of the available unsaturated lactones provides linear polymers which could then be ranked according to solvent resistance. Polymers of I were only slightly swollen by DMSO at >100°C whereas materials from II could be dissolved in warm DMF. The polymers from III were the least resistant and were soluble in chloroform. The synthesis of a difunctional monomer based on the α-methylene lactone group has been deferred because of the high priority given the project described below.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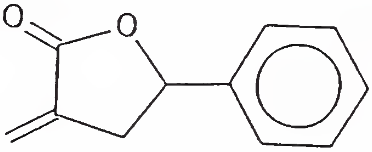
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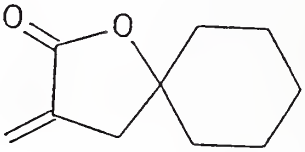
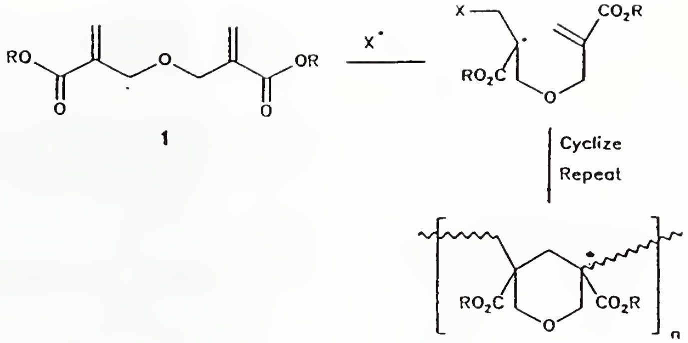

III

Cyclopolymerizable Monomers

The study of the recently developed oxy-bis-methacrylate monomers capable of undergoing a cyclopolymerization to yield polymers comprised of a cyclic ether repeat unit and pendant ester groups has been extended [37]. The efficiency of the synthesis of various ester analogs of this class of monomer has been significantly improved over the initial results. For example, the preparation of the diethyl oxy-bis-methacrylate has gone from an 8 day procedure with an 18% yield to a 1 day synthesis of 82% yield. Monomers with a variety of ester groups (Table I) have been prepared to compare the effect of the ester functionality on the synthesis and polymerization of these compounds. The monomers ranged from liquids to low melting crystalline solids.

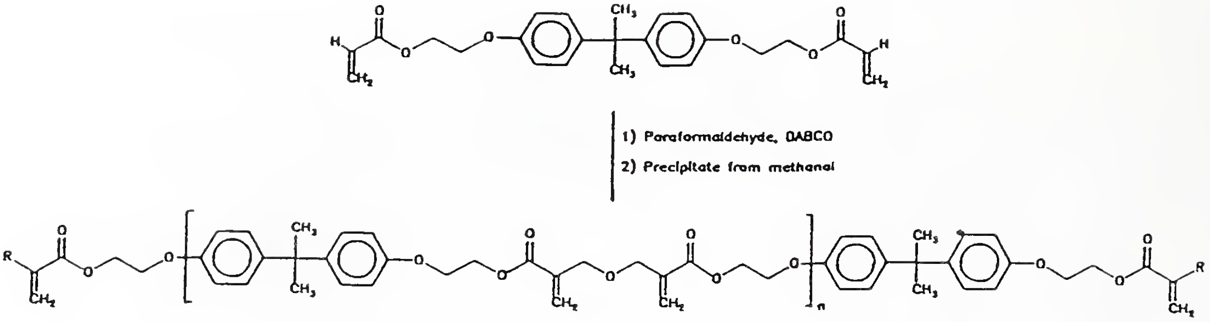
The results of the synthesis show that monomers with the larger ester groups required significantly more time to form than did those with non-bulky ester functionality.



The amount of side reaction products formed in the synthesis was also found to vary dramatically with reaction conditions and the identity of the ester group. In polymerizations, all the monomers were converted to completely cyclized homopolymers when dilute solution polymerization conditions were employed. In bulk polymerizations, all the polymers were crosslinked; however, the bulkier esters appear to yield polymers with a lower crosslink density. Solid state ^{13}C NMR analysis of the homopolymers produced in bulk indicated that extremely high conversions of 90-100% were achieved. The polymerization shrinkage of the cyclizable monomers is approximately 40% less than that observed for conventional dimethacrylates at comparable degrees of conversion.

As a result of the low shrinkage and high degrees of cure associated with these monomers, the formulation of the oxy-bis-methacrylates into composite resins was evaluated. It appears that the most appropriate utilization of these compounds involves the use of the liquid monomers to serve as diluent comonomers with conventional base monomers such as BIS-GMA. Attempts to use the bulkier oxy-bis-methacrylate derivatives as base monomers were less satisfactory due to the limited solubility of the crystalline materials. The excellent mechanical strength results obtained for the experimental formulations (Table II) demonstrate the compatibility of these new monomers with the conventional dimethacrylates.

The same chemistry which yields the difunctional oxy-bis-methacrylate monomers from acrylate starting materials has been applied to obtain multifunctional reactive oligomers from conventional diacrylates. For example an ethoxylated bis-phenol A diacrylate was converted to oligomer 2 in good yield and with a very simple purification procedure.



2

where R= —H or —CH_2OH

The oligomer can be polymerized to an extensively crosslinked network while the polymers produced appear to be less brittle in nature than those formed from crosslinked dimethacrylates, e.g. BIS-GMA. In composite resin formulations where oligomer 2 assumes the role of a base resin (ie., replacing BIS-GMA), materials with good mechanical strength are available, as shown in Table III. Other properties of these experimental formulations are currently under evaluation.

Table I

Synthesis and Properties of Oxy-bis-methacrylate Monomers

Ester, R	Compound	Yield, %	MP(BP), °C
Methyl	1a	65	47
Ethyl	1b	82	(85/13Pa)
Isobutyl	1c	74	(106/13Pa)
2-Phenethyl	1d	68	43

Table II

Diametral Tensile Strength of Photocured Composite Resins

Formulation	(wt ratio)	DTS, MPa ± SD (n)
BIS-GMA/1b	(75:25)	52.5 ± 2.2 (8)
BIS-GMA/1c	(70:30)	50.0 ± 1.8 (6)
1d/TEGDMA	(50:50)	48.3 ± 4.7 (6)
Control: BIS-GMA/TEGDMA	(70:30)	50.5 ± 1.3 (6)

Table III

Diametral Tensile Strength of Photocured Composite Resins

Oligomer/TEGDMA, wt. ratio	DTS, MPa ± SD (n)
75:25 (max workable viscosity)	49.4 ± 1.2 (6)
67:33	51.0 ± 0.9 (6)
50:50 (min workable viscosity)	48.9 ± 4.4 (5)

(g) Improved initiator systems for dental resins

No work has been done in FY89.

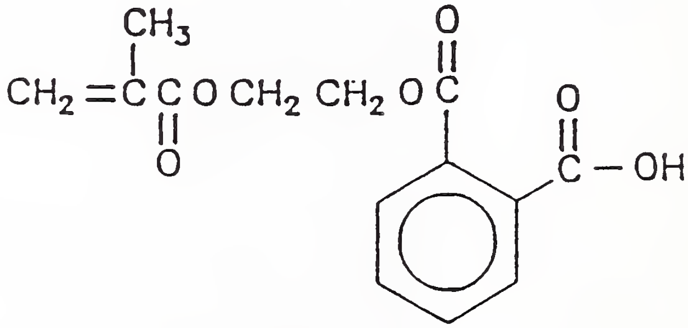
(h) Synthesis and Evaluation of Organometallic Monomers for Dental Applications (new)

Synthesis of Multivalent Metal Dicarboxylate Monomers

This study was designed to assess the feasibility of preparing multivalent metal dicarboxylate groups. Structurally PMDM (the diadduct of 2-hydroxyethyl methacrylate and pyromellitic dianhydride) is an ideal starting material for this study. Two basic routes were chosen to prepare these dicarboxylate monomers: 1) directly by the reaction of PMDM with stoichiometric amounts of the metal base [e.g. $Ca(OH)_2$] and 2) indirectly by double decomposition reactions of soluble alkali salts of PMDM with soluble multivalent salts (e.g. $ZrOCl_2$, $AlCl_3$) as shown in Figures 1, 2 and 3. PMDM salts were characterized by IR (see Figures 4 and 5) and, when soluble, by ^{1}HNMR. The Ca^{+2}, Mg^{+2} and, to a lesser extent, Zn^{+2} salts of PMDM were slightly soluble in water. Most other multifunctional metal salts (e.g. Cu^{+2}, Fe^{+3} Al^{+3}, ZrO^{+2}, Ti^{+4}) were insoluble both in water and common organic solvents. The aqueous soluble salts can be used to modify glass ionomer and similar cements (see Table IV). Salts containing redox metals can act catalytically in free radical initiator systems e.g. with t-butyl hydroperoxide plus ascorbyl or mercaptan containing compounds. Other potential uses include adhesive and/or coupling agents, reactive fillers etc.

A knowledge of the properties of some of these salts (e.g. Ca^{+2}, Al^{+3}, Fe^{+3}) may aid in the elucidation of the mechanism (s) of the Bowen adhesive system based on PMDM. A variety of metal containing monomers can be prepared from monomers with multifunctional carboxylic acid groups. A paper based on this work was presented at the 1989 IADR meeting [39].

A related study involved the synthesis of multivalent metal monocarboxylate salts of monomers containing only one carboxylic acid group. Mono-(2-methacryloyloxy) ethyl phthalate, MMEP (see below) was converted to the following carboxylate salts (Ca^{+2}, Al^{+3}, Fe^{+3}, ZrO^{+2}) which were characterized by IR and, when soluble, by ^1H NMR. The zirconate (ZrO^{+2}) salt of MMEP was prepared from $ZrOCl_2$ by methods B or B^1 (Fig. 3). This ZrO salt of MMEP is soluble in a variety of monomers, MMA, BIS-GMA, TEGDMA, etc., but insoluble in water. Composites based on ZrOMMEP containing resins have excellent esthetics and acceptable strength (DTS = 43-49 MPa). Also, resin systems contain zirconium or similar heavy metals have radiopacifying potential. Water soluble carboxylate salts of MMEP and PMDM (e.g. Ca^{+2}) also were made and may have applications in resin-modified polyelectrolyte cements, e.g. glass ionomer cements (see Table IV). An abstract based on this work has been submitted for the 1990 IADR.



MMEP

(i) Effect of post cure storage time on the properties of composites (new project)

In a previous study the time and temperature dependence of the microhardness (Knoop Hardness) and diametral tensile strength of four commercial chemically activated composites were investigated [40]. Other studies on commercial composites indirectly evaluated the extent and rate of polymerization these materials by measuring the Barcol hardness of the top and bottom of composite specimens after varying periods of irradiation and storage times [41, 42].

In this study the effect of post cure storage time (T) on the diametral tensile strength (DTS) of an experimental visible light activated composite was evaluated using the characteristic strength, S_o, and the Weibull modulus, m. The visible light activated resin contains BIS-GMA (70 wt %) TEGDMA (30 wt %), camphorquinone (0.2 wt %) and ethyl 4-dimethylaminobenzoate (0.8 wt %). The filler was a silanized silica glass (44 μm) containing BaO. The filler loading of the composite was 83.3 wt %. DTS specimens were 6mm D x 3 mm H. Ts' were 5 min., 15 min., 30 min., 60 min. and 24 hours (1440 min.), with specimens stored at 22°C in air. For each storage interval the number of specimens (n) was approximately 20. DTS specimens were fractured at a crosshead speed of 10 mm/min. The Weibull modulus m, characteristic strength S_o and the confidence intervals (CI) at 90% were:

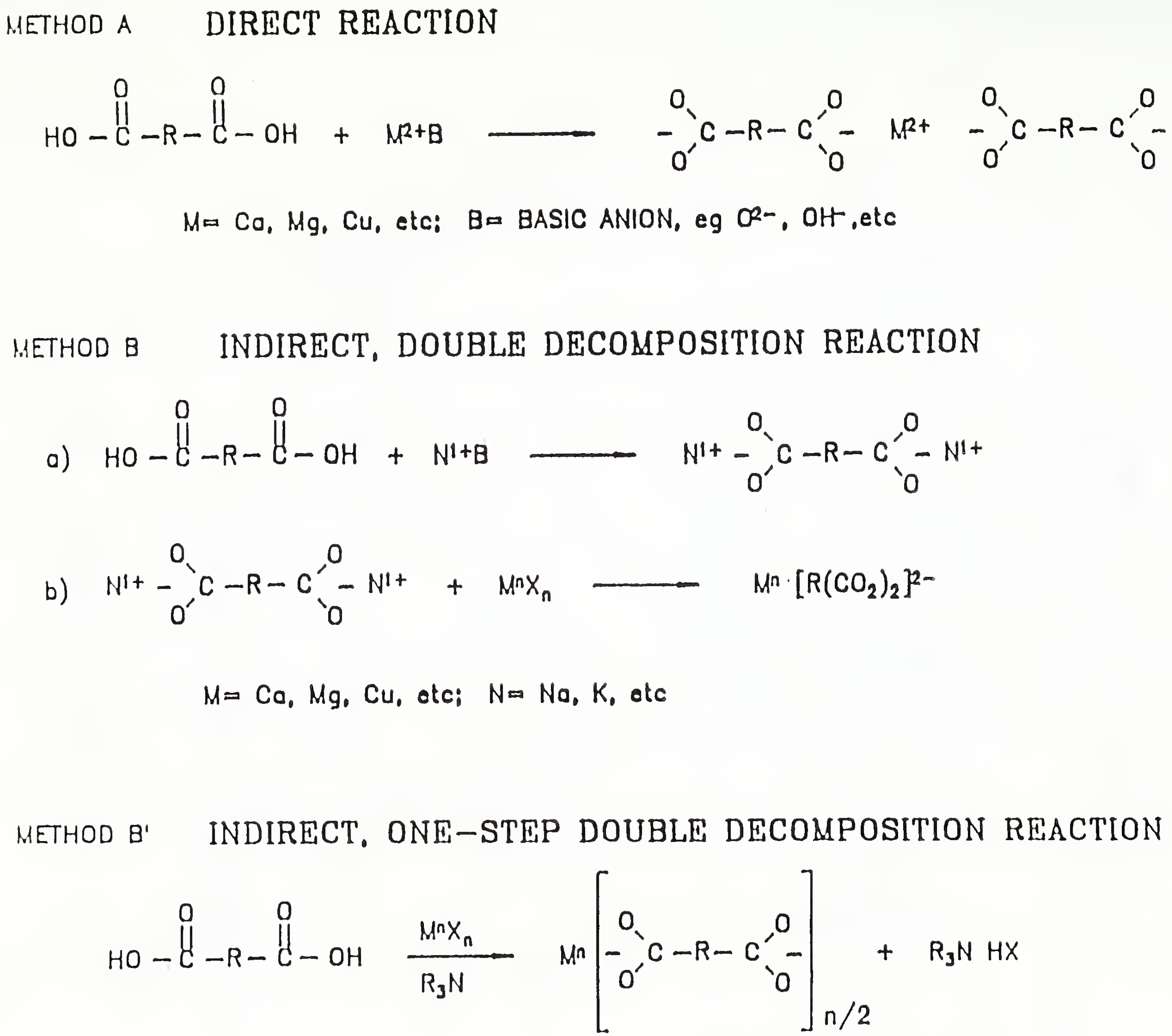
T (min.)	n	m	CI	S_o	CI
5	19	13.0	10.2-19.3	33.6	32.4-34.7
15	20	13.8	10.9-20.0	34.1	33.1-35.2
30	20	29.3	23.2-42.0	37.0	36.5-37.5
60	20	18.3	14.5-26.5	38.0	37.1-38.9
1440	20	22.1	17.5-32.6	43.6	42.8-44.4

It can be concluded that the Weibull modulus m is independent of the storage time; the characteristic strength shows a small, but significant increase between 15 and 30 min. and a much larger increase between 30 min. and 24 hours. (see Figures 6 and 7). An abstract based on this work was submitted for the 1990 IADR meeting.

(j) Determination of the water content of dental resins and composites using near infrared spectroscopy (NIR) (new project)

Important properties of resin based dental materials are their time-dependent water uptake and solubility characteristics. Gravimetric determinations of water in dental composites require long immersion and drying times to reach equilibrium and are complicated by solubility effects. The method described here measures the water content independently of solubility effects. It uses the 5200 cm^{-1} absorption band of water in the NIR (near infrared) region of the spectrum to determine the water content quantitatively in resin and composite specimens of .1 to .5mm thickness. The water concentration c[mol/L], with absorbance A in specimens of thickness ℓ[cm] can be calculated using Beer's Law: $A = \epsilon C \ell$. The absorptivity ϵ was estimated by (1) determining water sorption with a microanalytical balance of thoroughly dried polymer discs exposed to 100% relative humidity in a humidor at 37°C (to avoid any dissolution) and (2) relating the increase in water in the polymer to the increase in absorbance in the NIR spectrum. ϵ for water absorbed in a polymeric medium is inversely related to hydrophilicity and hydrogen bonding ability of the polymer and was constant over the narrow range measured. NIR and gravimetric measurements of water sorption of specimens exposed only to the atmosphere of a humidor (to prevent solubility) agree within 1%. Very thin specimens (.1mm) measurable only with the NIR technique equilibrate within a few days. Immersion of samples in water, resulting in some sample dissolution, allows the determination of sample solubilities by subtraction of NIR from gravimetric water sorption results. A paper based on this work was presented at the 1989 AADR meeting [43].

SYNTHESIS OF MULTIVALENT METAL CARBOXYLATES



METHOD A DIRECT REACTION

M= Ca, Mg, Cu, etc; B= BASIC ANION, eg O^{2-}, OH^-, etc

METHOD B INDIRECT, DOUBLE DECOMPOSITION REACTION

a)

b)

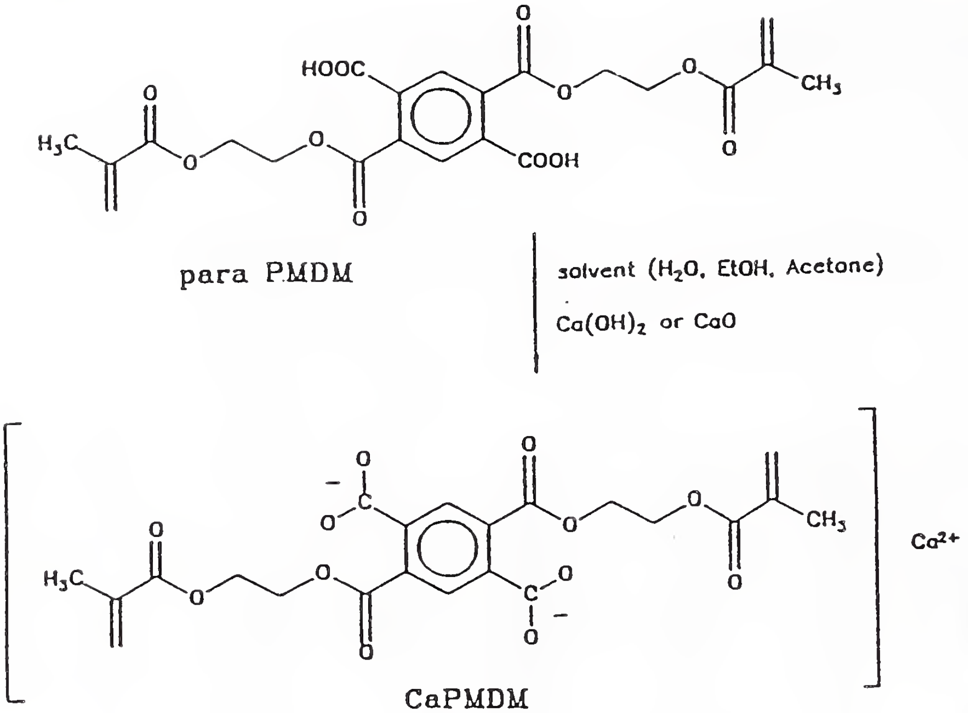
M= Ca, Mg, Cu, etc; N= Na, K, etc

METHOD B' INDIRECT, ONE–STEP DOUBLE DECOMPOSITION REACTION

Fig. 1

SYNTHESIS OF PMDM SALTS

METHOD A



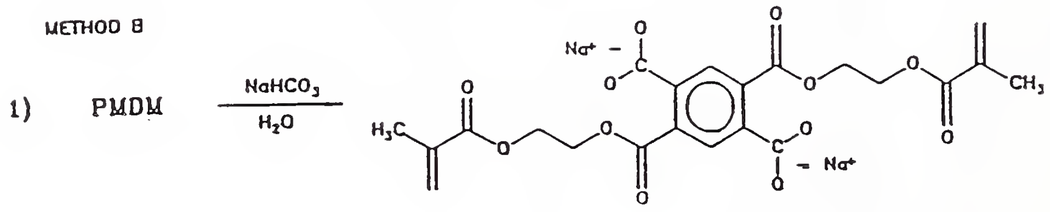
para PMDM

CaPMDM

Fig. 2

SYNTHESIS OF PMDM SALTS

METHOD B



$$2)\quad NaPMDM + AlCl_3 \xrightarrow[-NaCl]{H_2O} Al_2(PMDM)_3$$

METHOD B'

$$PMDM + ZrOCl_2 \xrightarrow[Acetone/H_2O]{Et_3N} ZrOPMDM + Et_3N\ HCl$$

Fig. 3

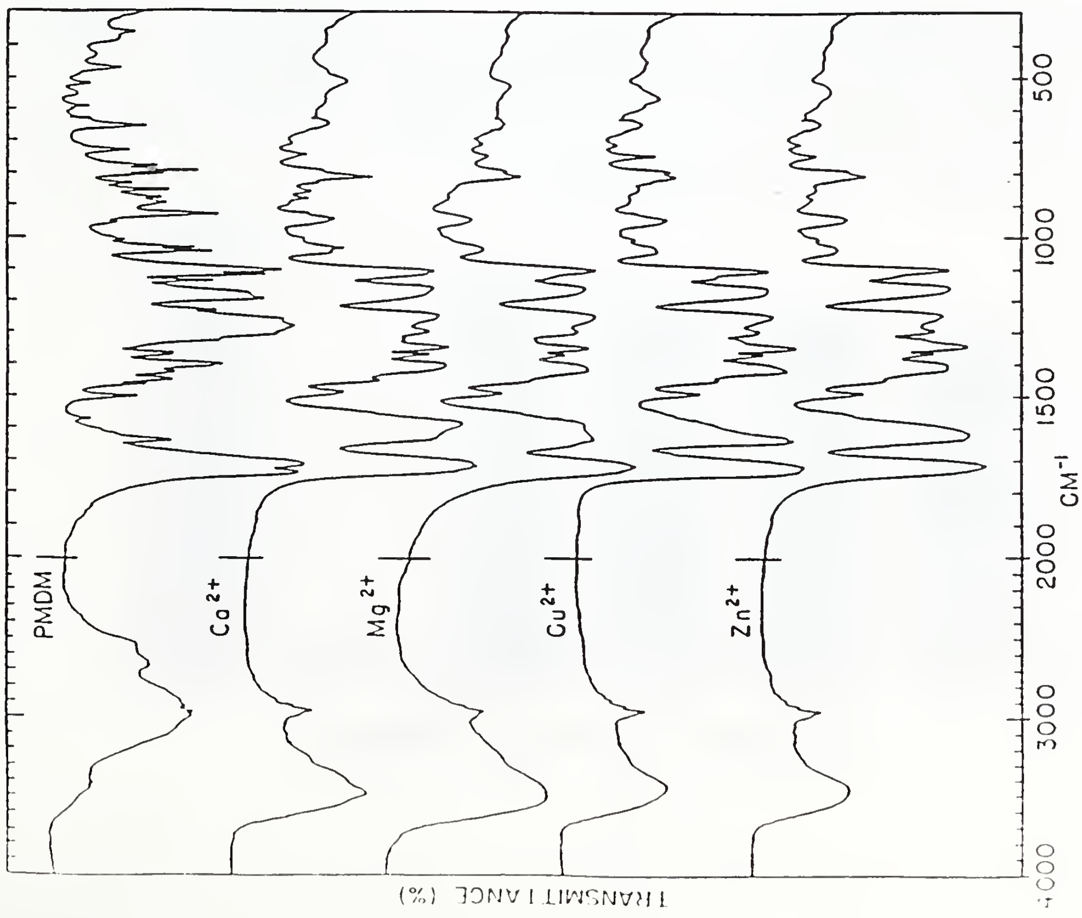

PMDM
Ca2+
Mg2+
Cu2+
Zn2+
TRANSMITTANCE (%)
4000
3000
2000
1500
1000
500
CM-1

Fig. 4

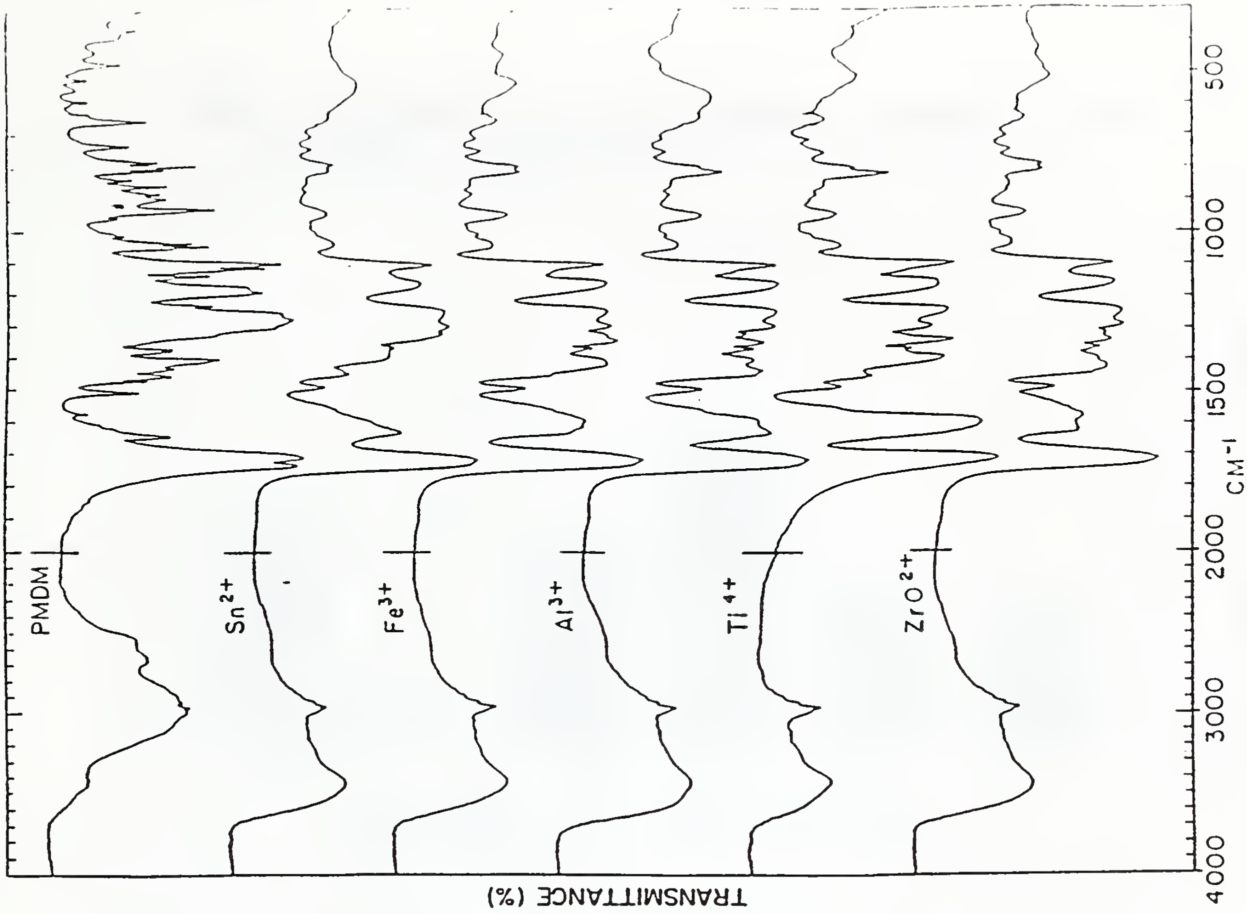

PMDM
Sn2+
Fe3+
Al3+
Ti4+
ZrO2+
TRANSMITTANCE (%)
4000
3000
2000
1500
1000
500
CM-1

Fig. 5

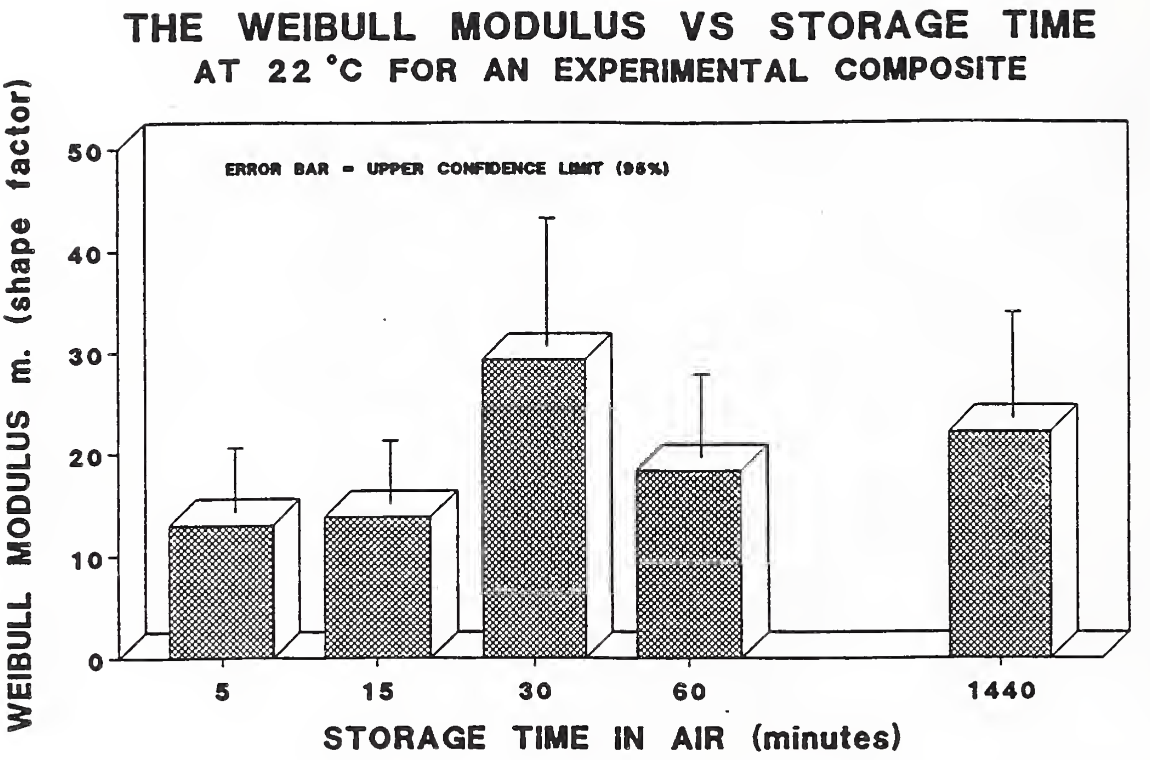

THE WEIBULL MODULUS VS STORAGE TIME
AT 22 °C FOR AN EXPERIMENTAL COMPOSITE
ERROR BAR = UPPER CONFIDENCE LIMIT (95%)
WEIBULL MODULUS m. (shape factor)
0
10
20
30
40
50
5
15
30
60
1440
STORAGE TIME IN AIR (minutes)

Fig. 6

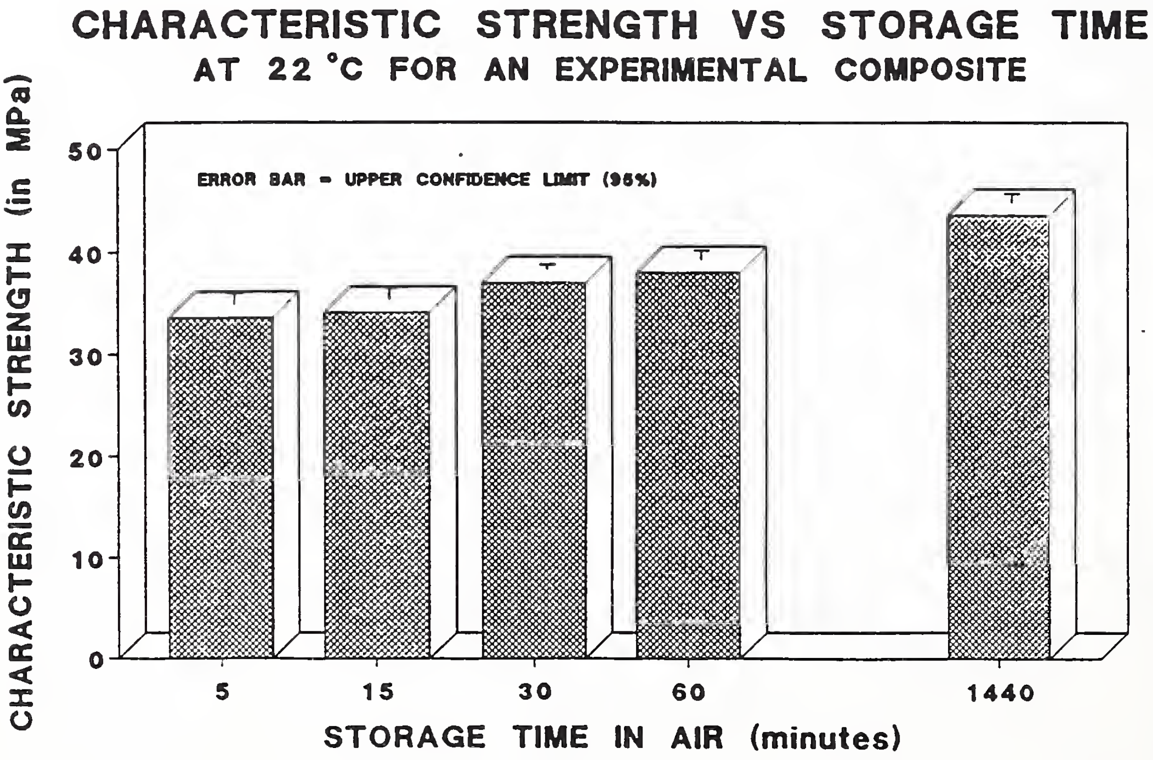

CHARACTERISTIC STRENGTH VS STORAGE TIME
AT 22 °C FOR AN EXPERIMENTAL COMPOSITE
ERROR BAR = UPPER CONFIDENCE LIMIT (95%)
CHARACTERISTIC STRENGTH (in MPa)
0
10
20
30
40
50
5
15
30
60
1440
STORAGE TIME IN AIR (minutes)

Fig. 7

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 certain optimal properties, especially biocompatibility, durability and adhesiveness. One approach for improving the overall properties of dental cements involves developing hybrid cement-composites or resin-modified cements. Of special interest are the glass ionomer cements, a class of 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 the system is relatively weak in either case because of the low tensile and flexural 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.

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 flexural strengths.

Phase I Formulation and Evaluation of New Cements

(a) Resin- and polymer-modified glass ionomer cements.

In addition to continuing the previously reported studies [44-46] on resin- or polymer-modified glass ionomer cements, we also investigated the use of water soluble carboxylate monomer salts (e.g. calcium methacrylate) as a means of modifying the properties of aqueous based cements. Table IV summarizes some of the results obtained using a water-hardening glass ionomer cement (Chemfil II, Detrey/Dentsply) and various vinyl carboxylate salts.

In a related study we examined the adhesive properties of resin- and polymer-modified glass ionomer cements to dentin and composite surfaces. We tested the tensile strength of a water-hardening glass ionomer (Chemfil II) versus several hybrid versions (obtained by appropriate modifications of the water and/or powder component) to both conditioned dentin (10% polyacrylic acid for 30 seconds) and composite (Silar; 3M; Group A: sanded and etched for 10 seconds; Group B: unetched, cured under glass slides). The seven modifications included 15% or 29% HEMA aqueous solutions activated by a free radical initiator system, aqueous solutions of a very high molecular weight poly(acrylic acid), PAA, molecular weight = 4 x 10^6; e.g. 0.5% PAA, 1.5% PAA, 0.5% PAA + 27% HEMA (with initiator system), and other aqueous polymer solutions. Samples were bonded, stored 24 hours at 37°C in distilled water and subject to direct tensile testing. One-way Anova and Scheffe's testing ($p \leq 0.05$) revealed that for bonding to dentin the only significant difference was between 15% HEMA (mean 1.57 ± 1.51 MPa, n=15) and 1.5% PAA (4.10 ± 2.02 MPa, n=15). The control (Chemfil II) was 2.52 ± 2.11 MPa, n=15. For bonding to composites no significant difference was found between etched (5.45 ± 3.77 MPa, n=15) or unetched (4.92 ± 1.52 MPa, n =15) controls. The 29% HEMA formulation unetched gave a tensile strength of 10.10 ± 1.24 MPa versus 4.49 ± 2.22 for the etched situation, n=15. Also the 0.5% PAA + 27% HEMA/unetched groups had significantly higher tensile strength (9.87 ± 2.76 MPa) than the unetched control. This study showed that acceptable bonding was achievable for most of the tested reinforced hybrid cements. Polymer-modified cements demonstrated higher bond strengths to composites when left unetched, with some having strengths superior to that of the control. An abstract based on this work has ben submitted to the 1990 AADR.

(b) Formation of Hydroxyapatite in Hydrogels from Tetra Calcium Phosphate Mixtures.

Previous studies showed that an apatitic calcium phosphate cement (CPC) forms under ambient conditions by the reaction of an equimolar mixture of tetracalcium phosphate (TTCP) and either anhydrous dicalcium phosphate (DCPA) or its dihydrate (DCPD) in H_2O or dilute aqueous H_3PO_4 [47,48]. Recently a study of the formation of hydroxyapatite and other phosphate products from the reaction of CPC mixtures in self-curing hydrophilic monomer systems was reported [49]. In this study the TTCP/DCPA reaction was studied in aq. solutions of water soluble polymers, e.g., gelatin poly(vinyl alcohol) and several poly(alkenoic acids), e.g., poly(acrylic acid). In gelatin and the nonionic polymer solutions, cement formation was observed with the formation of significant amounts of hydroxyapatite (HAp) within 24 hours. These cements had setting and strength properties similar to the original CPC, e.g., setting time (ST) ~30 min, compressive strength (CS) = 25-35 MPa. Significantly faster-setting and stronger cements were obtained using solutions of poly(alkenoic acids), e.g., ST = 1-2 min, CS = 54-81 MPa. However, only minor amounts of HAp were observed even after one month. With poly(alkenoic acids) as the liquid vehicle, rapid cement formation occurred also with just TTCP. The basicity of TTCP is sufficient to give a complex acid-base reaction with poly(alkenoic acids) analogous to that which occurs in forming zinc polycarboxylate cements from zinc oxide. A variety of potentially biocompatible TTCP/poly(alkenoic acid) cements can be prepared by varying the nature of the polyacid and the TTCP base powder mixture. An abstract based on the work has been submitted to the 1990 IADR meeting.

TABLE IV

24 HOUR DIAMETRAL TENSILE STRENGTHS[1] OF VINYL METAL CARBOXYLATE-MODIFIED GLASS IONOMER CEMENTS[2]

FORMULATION	COMPOSITION OF LIQUID (wt%)		COMPOSITION OF POWDER	POWDER/LIQUID	DIAMETRAL TENSILE STRENGTH IN MPa (Std DEVIATION)
1.	CaMAA[3] HEMA[5] DHEPT[6] NaPTsA[7] H_2O	8.6 18.6 0.2 0.1 72.5	CHEMFIL II POWDER ADMIXED WITH 0.3% BPO[4]	7	25.2 (3.9)
2.	CaMMEP HEMA DHEPT H_2O	10.5 27.5 0.4 61.6	CHEMFIL II POWDER ADMIXED 0.3 BPO	7	23.8 (3.3)
3.	Na_2PMDM 3-DMAB[8] NaPTsA H_2O	11.33 0.06 0.06 88.55	CHEMFIL II POWDER ADMIXED WITH 0.3% BPO	6	18.5 (1.7)
4.	K_2PMDM 3-DMAB NaPTsA H_2O	30.0 0.2 0.2 69.6	CHEMFIL II POWDER ADMIXED WITH 0.3% BPO	6	21.0 (3.5)
5.	MgPMDM HEMA GDMA DHEPT H_2O	2.9 31.1 4.7 0.4 60.9	CHEMFIL II POWDER ADMIXED WITH 0.3% BPO	7	23.4 (3.1)
6.	CaPMDM HEMA BIS-GMA TEGDMA HOOH H_2O	3.4 28.1 0.2 0.1 1.1 67.1	CHEMFIL POWDER ADMIXED WITH 0.2% ASCORBIC ACID AND 0.001% $CuSO_4 \cdot 5H_2O$	7	21.2 (2.7)
CONTROL	H_2O	100	UNMODIFIED CHEMFIL POWDER	7	20.7 (3.0)

---

1. N, NUMBER OF SPECIMENS = 6; 2. POWDER/LIQUID FORMULATIONS BASED ON CHEMFIL II 3. CaMMA = CALCIUM METHACRYLATE 4. BPO - BENZOYL PEROXIDE; 5. HEMA = 2-HYDROXYETHYL METHACRYLATE; 6. DHEPT = N,N-DIHYDROXYETHYL-p-TOLUIDINE. 7. NaPTsA = SODIUM p-TOLUENE SUFINATE; 8. 3-DMAB = 3-DIMETHYLAMINOBENZOIC ACID;

III. Improvement of 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 in 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 approximating those of the matrix, they can be used to form translucent fillings that match the normal 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 μm) averaging 0.04 μm 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 μm, but usually 2-50 μm), microfilled composites have smoother, more easily polished surfaces 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 [50-54].

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 [50,51]. 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 [52,53].

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 [55]. 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 with methacrylates [54,56].

Alkoxysilanes 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 [55]. 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 [54-56].

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 bifunctional silane agent 3-methacryloxypropyltrimethoxysilane has become the coupling agent of choice for use in glass filled dental composites. Their use is known to improve certain physical and mechanical properties. Only a few studies involving other types of bifunctional agents, e.g. titanates, have been reported in the dental literature [58]. Previous studies showed that zirconium (IV) dimethacrylate (ZrM) offered promise as a coupling agent for dental composites based on tricalcium phosphate [59] and calcium metaphosphate [60] respectively. In this study we evaluated three commercial organozirconium compounds, zirconium IV dimethacrylate, (ZrM) a neoalkyl trimethacrylate zirconate (NZ33), and a neoalkyl triacrylate zirconate (N239), as coupling agents for glass filled composites. The method chosen for evaluating the coupling efficacy of the zirconates was the diametral tensile strength (DTS) test using a composite based on a light-activated BIS-GMA resin with a barium oxide containing glass macrofiller (44 micron). Several techniques were used in applying zirconates: 1) pretreatment of filler, 2) integral blending (IB), using minor amounts of zirconates dissolved in resins with untreated glass (UG), and dual treatments (DT) which combine 1) and 2). The DTS values for composites with 83.3 wt% pretreated glass were: 0.3% ZrM-33.9(1.6)MPa; 1.5% NZ33-36.2(2.2)MPa and 1.0% NZ39-37.9(1.8)MPa compared to 26.4(3.7)MPa for the UG composite. The DTS of a similar silanized glass (SG) composite was 55.4(3.2)MPa. Using 1.7% N233 in the resin (IB) and UG resulted in similarly filled composites with a DTS=32.2(1.4)MPa, indicating that IB was less effective than pretreatment of the glass filler. DT using small amounts of ZrM (0.25% and 1.24%) in the resin with ZrM treated glass and SG gave DTS values of 34.12(2.8) and 56.4(2.9)MPa, respectively. An abstract based on this work has been submitted for presentation at the 1990 AADR meeting.

IV. Bonding of New Resin Systems to Tooth Structure

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

Current resin-based dental composites do not adhere 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 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 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]. Many of the dentin bonding systems are complex, including several steps, indicative of the problems of adhesion to this heterogeneous substrate. The mechanism(s) of bonding are still not completely understood.

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 (e.g. N-phenylglycine (NPG) and N-p-tolylglycine (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, urea or Schiff base formation. Another approach for chemically bonding to collagenous substrates involves graft polymerization techniques using free radical initiation [7-16].

Recently, several 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 [14]. The second bonding system is based on the functional monomer, 4-methacryloxyethyl trimellitic anhydride (4-META) and a pretreatment of dentin with a ferric salt such as ferric citrate [9,10]. The third bonding procedure utilizes a brief application of a cleanser, mordant aqueous solution of ferric or aluminum oxalate, a surface active agent (e.g. NPG, NTG) or 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. A commercial adhesive, Scotchbond 2, which consists of an acidic primer (and aqueous solution of HEMA and maleic acid) and a monomeric bonding system based on BIS-GMA and HEMA seems to adhere by a micromechanical bonding via a resin reinforced surface layer of treated dentin [61].

PROGRESS REPORT

Phase I. Synthesis of Carboxylic Acid-Containing Monomers for Bonding to Tooth Structure.

An adhesive system for the bonding of composites to dentin based on a 10% acetone solution of the solid monomer PMDM (the para isomer of the adduct of PMDA, pyromellitic dianhydride and hydroxyethyl methacrylate) has been described. The SBS [shear bond strength in MPa] of the related systems PM-GDM (a liquid mixture of isomers prepared from PMDA and GDM, glycerol dimethacrylate) and PM-TEG (PM-GDM modified with TEGDMA, triethyleneglycol dimethacrylate) has been evaluated using Weibull analysis.

Volume and conc. of monomer in acetone solution	SBS	s.d.	SO	CI (SO)	m	CI (m)	n
1 drop 10% PMDM	12.7	1.2	13.7	11.5-16.4	2.1	1.6-2.7	25
1 drop 10% PM-GDM	11.3	1.1	12.4	10.4-14.9	2.5	1.8-3.4	18
2 drops 23% PM-GDM	18.5	1.0	20.6	18.2-23.3	3.1	2.4-4.1	24
2 drops 23% PM-TEG	21.7	0.9	23.1	21.5-24.8	6.2	4.5-8.4	19

n = number of specimens; s.d. = standard deviation

Vertical lines group nonsignificant differences, shown for SBS by a ranking test (Kruskal-Wallis) and by Weibull analysis for the 90% confidence interval, CI, of the characteristic strength, SO, and Weibull modulus m. PMDM and PM-GDM gave very similar values of SBS when applied in thin layers. Because PM-GDM is a liquid, it could conveniently be applied in a thick layer which led to higher mean SBS and SO. Moreover, modification of PM-GDM with 10% of TEGDMA doubled the Weibull modulus m, which indicated a narrower range of failure and thus higher reliability of the bonding system. An abstract based on this work was submitted for the 1990 IADR.

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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 NIST 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, volume dilatometry profilometry, 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 facilitate the development of improved prototype composite restoratives here and at other laboratories, and, in some cases, to assess the extent of wear on the opposing enamel when the restorations are placed in stress-bearing occlusion (Class I and II).

This task is comprised of the following sections:

A. Wear and Durability Assessments of Composite Restoratives

Phase I. Recent Commercial Composites Which Appear Promising for Posterior Occlusal Application. (not active this period).

Phase II. Experimental Composites with Flexible Polymers. (not active this period).

Phase III. Glass-Ionomer Cements: Conventional, Metal Filled, and Modified Experimental.

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

Phase V. Experimental Studies on Experimental Composites Employing Apatite Reinforcing Fillers (not active this period).

B. Assessment of Wear of Human Enamel Against Dental Restorative Counterfaces.

Phase I. Assessment of Wear of Human Enamel Against a Conventional Porcelain and a New Castable-Ceramic Counterface.

Phase II. Wear of Hydroxyapatite Against Dental-Alloy Counterfaces.

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

Phase I. Determination of T_g as a Function of Cure Temperature (This phase cannot be continued).

D. Wear Instrumentation (New Task).

Phase I. Methodology for Improved Wear Apparatus.

Phase II. Selection, Acquisition, and Assembly of Electronic Components.

Phase III. Completion of Apparatus, Including Design and Assembly of Mainframe, (Drive Units, and Transducer Components.)

A. Wear and Durability Assessments of Composite Restoratives

Background

Clinical data and microdefect analyses of *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 and accelerated 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 (usually for 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 decreases in microhardness, which usually corresponded to enhanced wear [1,2]. 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 *in situ* temperature (37°C). With the free-radical activated processes, the increase in 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 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 [3,4]. The degree of cure was enhanced by simply elevating the cure temperature.

Since a sufficient elevation in temperature would be impracticable for *in situ* 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 integrity and corresponding leakage in application.

Accordingly, there are three important criteria to be satisfied for an appropriate matrix resin. These are (1) low solubility parameter (below the range of liquid food ingredients), (2) a high degree of cure (at in situ temperature) to further limit diffusion of liquids and subsequent swelling, and (3) low polymerization shrinkage to maintain marginal integrity. 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). The polymerization shrinkage was reduced by using the prepolymer of PFUMA having about 10 repeat units which would correspond to molecular weight of 12,060 g/mol.

A composite comprising a more flexible resin, polyfluoromethacrylate (PFMA), and other diluent monomers along with a photoinitiator for visible-light activation in addition to solely chemical (as with the PFUMA system) was formulated and evaluated. The results for the PFUMA and PFMA systems are summarized in last year's annual report [27] and references [5,6].

The inorganic reinforcing filler was evaluated by preconditioning commercial dental composite specimens in weak intraoral acids which may damage the filler at 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 corrosion plays an important role in the degradation of composite restorations as evident from the leaching experiments of Söderholm [7,8] and the wear and hardness measurements made at NIST [9]. The reason for including Phase V (apatite fillers) was to determine if present radiopaque fillers could be replaced by apatite fillers combined with certain alkaline-earth elements to achieve radiopacity. It is expected that the apatite fillers will be less sensitive to corrosion from intraoral fluids [10].

Since glass-ionomer cements show good bonding properties to dental tissue [11], 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. 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 [12]. Specimens preconditioned in dilute lactic acid revealed considerable chemical dissolution as apparent from electron micrographs and accelerated wear. More recent work [13] on a commercial silver-sintered 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 stressed the need for appropriate modification in the composition and structure of this class of materials for enhanced durability.

The so-called hybrid cement-composites (HCC) formulated at NIST were 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 (For further details, [27]). After mixing, the two reactions (polymerization of HEMA and hardening of the 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 fracture 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 [5].

Another specific source of damage to dental composites is from the application of topical fluoride agents which may eventually reach restorations even though not applied to them directly. In this connection, collaborative efforts were started with the University of Maryland Dental School at Baltimore to determine the effects of various topical fluorides on degradation and wear of composite resins.

Very accurate weighing measurements and microdefect analyses revealed that, some damage resulted on the composites from gel treatments. Little or no significant changes resulted in the wear rates. The experimental results are summarized in references [27] and [18].

PROGRESS REPORT

Phase I. Recent Commercial Composites Which Appear Promising for Posterior Occlusal Application. (not active this period)

No experimental activity in Phase I was undertaken during this reporting period. Our past work on commercial composites provided a sufficient basis to initiate research on NIST experimental composites. At a later time we will very likely conduct some evaluations of other selected commercial posterior composites for fundamental information.

Phase II. Experimental Composites with Flexible Polymers (not active this period)

The results of the performance evaluation of the dual-cured, flexible-resin composite described earlier were presented before the IADR Conference in March 1988 [14]. At the same meeting, a paper given by Ellison [15] described results from clinical trials involving restorations of composites containing PFMA resin. The investigators observed more deterioration of anatomic form and marginal discoloration over one year than what is normally observed for BIS-GMA based resins over the same period. Although their specimens were prepared differently from ours, we believe that the principal limitation on the performance of this kind of restorative results from the low degree of cure. We originally thought that the flexible resins would reach a higher degree of cure because of their flexibility; however, their affinity to oxygen, which competes with the cure process, seems to offset the advantage of flexibility. In future studies employing fluorinated resins, we believe that either we have to find a way to keep oxygen (air) out during processing or incorporate a scavenger to absorb oxygen before, and during, polymerization.

Phase III. Glass-ionomer Cements: Conventional, Metal-Filled, and Modified Experimental. (task completed)

No additional wear or environmental resistance studies on glass-ionomer cements have been undertaken during this reporting period. We believe that we have met our objectives with the hybrid cement-composite and are now considering the possibility of implementing some clinical tests. A separate study of margin leakage of this material employing the sandwich method [16] with the silver nitrate staining technique [17] revealed favorable results. A manuscript describing the wear and environmental resistance studies is essentially completed and will be submitted to WERB. A patent application on the hybrid cement-composite has been submitted.

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

The activity on the effect of topical fluoride treatments on commercial dental composites principally involved preparation of manuscripts for publication. A paper summarizing the later results was presented by Katherine Kula (University of Maryland) at the ADA Annual Session, Honolulu, Nov. 1989.

Phase V. Experimental Studies on Experimental Composites Employing Apatite Reinforcing Fillers. (not active this period)

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

Some work has been initiated, however, on the preparation of apatite and phosphate fillers in collaboration with the American Dental Association at NIST. If these appear to be promising, some wear and environmental resistance studies on corresponding composites may be conducted during the next reporting period.

B. Assessment of Wear of Human Enamel Against Dental Restorative Counterfaces

Background

Of increasing concern is the extent of wear on human enamel caused by occlusion with opposing restorations [19]. In our *in vitro* wear studies on commercial composites we found that the conventional composites with large rough particles, although not intended for occlusal applications, produced the most wear on the wear pins. It was encouraging to note, however, that the posterior microfills produced the least amount of wear among the composites tested. The wear on enamel from opposing composite restorations has been determined to depend upon the hardness and roughness (filler particle size and shape) of the composite [19]. In this connection an acceptance standard has been proposed by Lambrechts et al. [20] with respect to surface roughness, which is an indication of increased concern of this problem with respect to composites and other restoratives. In some of our work we are in the course of evaluating enamel wear resulting from commercial dental alloys and ceramics.

PROGRESS REPORT

Phase I. Assessment of Wear of Human Enamel Against a Conventional Porcelain and a New Castable-Ceramic Counterface.

In collaboration with the Naval Dental School (NDS) wear measurements on human tooth enamel against rotating counterfaces of a conventional porcelain and a new castable ceramic have been made employing fresh distilled water as a medium. Contrary to what was expected, the castable ceramic (Dicor), glazed with shading porcelain according to the manufacturer's specifications, produced more wear on the conical enamel pins than the unglazed ceramic. There was no significant difference between the enamel wear resulting from the unglazed ceramic and the porcelain. Accordingly, the conclusion from this study is that the shading should not be used in areas that will articulate against opposing teeth.

The results of this preliminary study were presented at the IADR Conference in March 1988 [21]. A manuscript has cleared WERB and has been submitted to the Journal of Prosthetic Dentistry.

During this reporting period it was realized that the data could be deficient or perhaps, nondefinitive, for two reasons: (a) Insufficient data were obtained to clearly differentiate between the results for the glazed and unglazed ceramics, and (b) It is not clear that distilled water is an acceptable substitute for human saliva in this particular case. Accordingly NDS and NIST have decided to conduct additional work at our laboratory in an attempt to further delineate these results. The new tests will include constant immersion in both distilled water and a synthetic saliva (Xero-Lube, Scherer Laboratories, Inc., Dallas, TX). Experiments involving two NDS residents are currently in progress at NIST.

Phase II. Wear of Hydroxyapatite Against Dental-Alloy Counterfaces. (task completed)

Recently, wear studies were made involving the wear of synthetic hydroxyapatite (to simulate enamel) discs resulting from wear pins made of certain commercial dental alloys and commercially pure (CP) titanium. The wear of the hydroxyapatite did not necessarily increase with increasing pin hardness, as might be expected. In fact, some of the very hard alloys tended to polish the counterfaces producing very low wear rates. In some cases two distinct types of wear were observed (1) a surface pitting on the hydroxyapatite, which produced a constant wear rate on both pin and disc and (2) a "glazing" of the hydroxyapatite which corresponded to an essentially zero wear rate. These results suggest that the nature of the hydroxyapatite surface may be a dominant factor in determining the wear rate and, in some cases, be more significant than the type of alloy counterface.

An abstract covering these results has been presented at the 1989 IADR Conference.

C. Glass-Transition Temperature (T_g) of Matrix Polymers (not active this period)

Background

The glass-transition temperature, T_g, in particular as a function of cure temperature, is an important parameter to facilitate the evaluation of the performance of resin-based composites. With free-radical activated systems, the degree of cure is limited by a critical viscosity at which the molecular motion effectively ceases, thus prohibiting further proximation of reactive species, which essentially terminates the curing process [22]. Since T_g is a manifestation of an isoviscous state, the viscosity depends upon T_g, which, in turn, depends upon the cure temperature. If the cure temperature is increased sufficiently, complete conversion may be obtained (at least in principle) for which the corresponding T_g is designated $T_{g\infty}$. For the flexible polymers, the value of $T_{g\infty}$ is low in comparison to that for a rigid polymer. Thus for the flexible polymers, T_g at the *in situ* cure temperature and $T_{g\infty}$ will be closer together which is tantamount to a higher degree of cure. On the other hand, although a value of $T_{g\infty}$ very close to the *in situ* cure temperature will produce a high degree of cure, the matrix will be too compliant mechanically to be useful as a restorative material.

PROGRESS REPORT

Phase I. Determination of T_g as a Function of Cure Temperature

(This phase cannot be continued).
Using the Weisenberg rheogoniometer, the cure temperature dependence of T_g has been determined [23] for pure BIS-GMA and 70/30 BIS-GMA/TEGDMA, both of which, especially the former, are rigid-polymer systems and, thus, have large values of $T_{g\infty}$. The principal reason for no activity on this project during this reporting period was that the equipment used belonged to a different laboratory. At their request, the equipment was returned before our work was completed.

D. Wear Instrumentation (New Task)

Background

The in vitro wear measurements mentioned throughout this chapter were made using a pin on disc apparatus described in Reference [24]. The original version was designed and assembled at the University of Indiana [25]. 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 [24]. This modification resulted in a more convenient, flexible, and reliable system, which has been used up to the present time. Over the past several years considerable activity was devoted to the design, acquisition, and construction and assembly of components to obtain a new and improved version of a pin and disc wear apparatus, which was completed near the end of this reporting period. The salient features are described below.

PROGRESS REPORT

Phase I. Methodology for Improved Wear Apparatus

As a consequence of increased demand and new methodology in dental wear measurements, a new pin on disc wear apparatus was designed and assembled. The new version has independent stepping motors as drives for the three 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.

As with the precursor, track-depth measurements using linear variable differential transformers (LVDT) may be taken at ten fixed positions around the track circumference to obtain a reliable average; however, by virtue of the stepping motors, this number also will be programmable.

A distinct advantage over the previous system is that the forthcoming one will allow wear testing under arbitrarily selected media.

The computer, which controls the apparatus, has the capability to do calculations for data processing including statistics, and thus will not require manual transfer of the vast amount of data acquired during each wear run to a different device.

Phase II. Selection, Acquisition, and Assembly of the Electronic Components.

Most of the commercially available electronic components for the new wear apparatus have been acquired and tested during previous reporting periods. These items include the computer (programmable in BASIC), hard and soft disc drives, a printer, and a data acquisition control unit, which comprises an integrating voltmeter, a 20-channel relay multiplexer with thermocouple compensation, a 16-channel general purpose switch, an 8-channel power controller, a 3-channel counter, and a stepping motor controller. The counter, one for each of the rotors, which may be running at different speeds, measure the number of disc revolutions by counting pulses from the LED's (light emitting diodes). These measurements ascertain the total wear-track length for each disc.

The stepping motors, their DC power supply and control circuits, and LVDT's and conditioning circuits, pulse-interrupt circuit, and GPIB (general purpose interface bus) interfaces have been acquired, or designed and constructed during the last reporting period. The stepping motor drivers were finished and implemented during this period.

Phase III. Completion of the Apparatus, Including Design and Assembly of the Mainframe, Drive Units, and Transducer Components.

The mainframe, which is the mechanical portion of the apparatus including the drive motors and rotating disc assembly, the pin assembly, wear measurements assembly, and cam lifting assembles for the pin and measurement devices is now complete. All interconnections have been made, initial computer programming has been done, and, hence, the system is operational. The only additional work yet to be done (aside from actual wear measurements) involves more sophisticated programming which will be determined from the kinds of wear measurements to be undertaken.

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III DENTAL ALLOYS, CERAMICS AND METROLOGY

Overview

Wide fluctuations in the costs of dental restorative precious metal alloys have ensued over the past ten years. At the same time new materials for fabrication of non-metallic restorations have been introduced as have alloys of various kinds for cast metal restorations. The new materials can vary considerably in their fabrication characteristics and clinical performance. More reliable methods than now exist are needed to evaluate properties and develop methods to aid in prediction of clinical performance. For porcelain-fused-to metal alloys the prime factors include thermal-stress compatibility, porcelain-metal system strength, alloy castability and the attendant capability of producing good fitting castings. Metrology plays an important role as the significance and relevance of materials properties needs to be more fully addressed in terms of relationships to clinical performance, reliability and predictability. Any measurement technique or process that can affect material properties or interpretation of clinical diagnoses rightfully belongs in this category.

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 was undertaken to clarify the parameters which are most important in developing residual stress. These can include the thermo-plastic properties of the porcelain, thermal conductivities, temperature dependent elastic moduli, glass transition temperatures (porcelain) and coefficients of thermal expansion of porcelains and alloys.

Accomplishments

The objective of this part of the investigation was originally to explore the potential of using the gap of a porcelain veneered split metal ring as a means for determining the thermal stress compatibility between porcelain and metal [1,2]. As this project has progressed that objective remains in view; however, the plan has been expanded to explore the use of reliability analysis for prediction of fast-fracture compatibility. This will utilize finite element modeling (FEM), and use of the Weibull fracture stress distribution for risk-of-rupture analysis.

Phase I. Complete Development of the Required Finite Element Model (FEM) for Stress in Porcelain and Porcelain-Metal Slabs.

This phase is completed. (see NBSIR 88-3782)

Phase II. Calculated effects of variables included in Phase I on stress distribution.

This phase is completed (see NBSIR 88-3782). A manuscript entitled "Transient and Residual Stresses in Dental Porcelains as Affected by Cooling Rates" has been published.

Phase III. Proceed with the Input of Metal Properties for Part of the FEM and Complete the Input of Material Parameters.

This phase has been completed. The results of the modeling are discussed under Phase IV.

Phase IV. Devise a Simple Analytical Representation of Stress-Strain for Porcelain-Metal Systems, if Possible for a Split Ring.

This phase has reached the stage wherein one manuscript entitled "Transient and Residual Stress in a Porcelain-Metal Strip" has been submitted for publication. Because the complexities involved using the effects of cooling rates on glass transition temperatures and temperature distributions, many possible combinations of thermal expansion coefficients, temperature dependencies of porcelain shear viscosities, etc., a simple analytical representation of stress-strain is not considered possible. An empirical representation for either surface or porcelain-metal interfacial stress was found from the computer modeling:

$$\sigma = k(q/q_o)^n \qquad \text{eqn. 1.}$$

where σ = stress; with k, n, empirical constants dependent on thickness and the porcelain and metal properties; q is the cooling rate and q_o is a reference cooling rate.

A further result of the study shows the following relationship between curvature, ρ, of the porcelain-metal beam and cooling rate:

$$1/\rho = D\ (q/q_o)^m \qquad \text{eqn. 2}$$

where D and m are characteristic constants for a beam of given materials and thicknesses.

Phase V. Compare the Results of FEM vs. the Theory Developed by Scherer [3] for a Simpler Porcelain-Metal System.

Scherer (3) has pointed out that in the case of viscoelastic materials the curvature of a bimetallic strip or split metal ring may not be expected to vary linearly with differences in thermal expansion between the two materials (as would be the case for elastic behavior). Scherer notes that the viscoelastic model "permits a rational interpretation of expansion mismatch "in split ring" and sandwich seals, but that the curvature is not a linear function of the elastic mismatch. The results from our model agree in this sense; combining equations 1 and 2 from Phase IV we find the residual stress in either the surface or interface is represented by equations of the form.

$$\sigma = k\ (\rho D)^{-n/m} \qquad \text{eqn. 3}$$

It is clear that stress does not vary linearly with curvature as would be expected from the elastic calculations. Further, the ratio n/m lies between 2 and 7; hence, stress is much higher than would be expected from the elastic analogue. This is not surprising as stresses are produced from thermal gradients as well as stress relaxation from viscoelastic behavior. Scherer neglects the effects of thermal gradients in his calculations so his results should only come into reasonable agreement for slow cooling rates where thermal effects are not important. Because stress is so highly dependent on curvature (with $n/m \sim 2$ for the interface and $n/m \sim 7$ for body surface porcelain) measurement of curvature is not a sensitive indication of surface layer stresses. These results also show rapid cooling as having a much stronger effect in producing beneficial residual compressive stresses in the surface versus the production of detrimental interfacial stresses.

Phase VI. Extend the Results of FEM and Those from Part B (Following) on Porcelain-Alloy Compatibility to Risk-of-Rupture.

This is a new phase. The possibility exists that risk-of-rupture will be more meaningful than compatibility. At the time of this report this phase is being postponed in order to make further use of the models already developed for porcelain and porcelain fused-to-metal for explaining relaxation behavior of those systems under externally applied loads at temperature.

B. Porcelain-Alloy Compatibility: Strength of Porcelain-Metal Systems

Overview

The development of a porcelain-fused-to-metal (PFM) beam for the evaluation of PFM system strength under tension in four point bending has provided a quantitative means of assessing the effects of various manipulations on the overall PFM system strength.

The manipulations to be evaluated are: 1) the effect of reglazing on a dental porcelain, 2) the effect of adding alumina to a porcelain composition (which alters the residual stress in the PFM system), and 3) the effect of submersion of the specimen in water for one week on the overall PFM system strength.

PROGRESS REPORT

Specimen preparation has been completed for the first 2 items to be considered.

Phase I. The Determination of the Effect of Porcelain Reglazing on System Strength.

This section has been completed (see NBSIR 88-3782, 1988)

Phase II. Evaluation of System Strength as Affected by Flaws.

The work on the reglazing of fractured porcelains with four point bending of a PFM beam has been completed and presented at the IADR general session in March 1988 [4].

The modified porcelain (filled with alumina) was prepared and the coefficient of thermal expansion was determined as $5.5 \times 10^{-6}/°C$. A total of six specimens were made for the determination of the PFM system strength using the modified porcelain; however, all specimens showed spontaneous fractures upon cooling from the glazing cycle. A continuation of this work is being considered; however, at present it appears of lesser importance relative to some other projects reported on here, such as: plasma sterilization, the use of Weibull statistics in analysis of the properties of materials and the effects of environment on the strength parameters of dental composites.

Phase III. The Effect of Submerging the Samples in H_2O for One Week Prior to Fracture.

This phase is planned to follow Phase II, however work in this area is delayed due to concentration of efforts in other areas as noted in Phase II.

Phase IV. The Effect of "Rounding the Corners" of the Specimen at the Side of the Specimen.

Preliminary results show that the extent to which corners are rounded does not appear to affect the PFM strength, but more data are needed.

There may be a difference between results with rounded corners and right angle sharp corners; the results are inconclusive at this stage due to very limited data. There also needs to be a reassessment of the usefulness of this test method based on a perceived need for more extensive finite-element modeling of the 4-PT bend specimen.

With the addition of M. Chiang to the group's efforts, more sophisticated analyses of stresses within multimaterial systems are being conducted with a view toward new adhesive bond test methods as well as system strength determinations.

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

PROGRESS REPORT

Overview

Because of the many dental alloys appearing on the market there exists 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. These have been discussed in NBSIR 86-3320.

A primary effort at NIST 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 employing a polyester-grid mesh pattern has been chosen. (see NBSIR 87-3539, 1987 for more details).

Accomplishments

This study has now virtually been completed. (see NBSIR 88-3782). A manuscript entitled "Mesh Monitor Casting of Ni-Cr alloys; Element Effects" is scheduled for publication within the calendar year 1989 in the Journal of Dental Materials.

D. Castability (Accuracy of Fit of Dental Castings).

Accomplishments

An experiment on the thermal expansion of a phosphate bonded investment has been performed using a total of 10 specimens. The findings indicate a change in strain which reproducibly coincides with the onset of the phase change in the filler of the investment. The observed expansion, even though reproducible both on heating and cooling, is of such magnitude (20% net strain) that it most likely is an electrical phenomenon that is temperature dependent.

The strain gauges, as they are currently available for high temperature investigations, are not suitable for embedding in casting investments.

This project has been terminated, with one manuscript having been published Meiser et al., J. Prosthet Dent 53(6): 870-873, June 85 and another accepted for publication in J. Prosthet Dent entitled "Multidimensional Internal Setting Expansion a Phosphate-Bonded Casting Investment Measured with Strain Gauges".

E. Solderability

This project has been discontinued as explained in a previous report NBSIR-87-3539, 1987.

F. Metrology and Analysis: Measurements for Characterization of Dental Materials

All current work related to this section is reported in section H which deals with relationships between metrology and clinical performance.

G. Metrology and Analysis: Occlusal Force Indicator

No actual development of the occlusal force indicator took place using the piezo-electric polymer polyvinylidene fluoride (PVDF).

During May 1988, W. de Rijk attended a seminar by the research staff of Tekscan Inc., the manufacturer of the T-Scan system for occlusal force measurement. The T-Scan is a system which uses a thin (60 micrometers) wafer as a transducer and has a PC-AT type computer for data gathering and processing. The instrument has only very recently been introduced and is conceptually similar to the system suggested in our initial proposal. The transducer in this system is based on the change in electrical resistance in a carbon filled polymer. The signal processing unit as made by the company is more than adequate, but the clinical effectiveness of the transducer could be vastly improved with a bite wafer that is thinner and that has less rigidity. The current assessment is that the T-Scan system could be significantly improved if a PVDF transducer of less than 10 micrometers thickness and low rigidity could be made.

Due to concentration of efforts on other areas described in this report no progress was attempted, especially in view of the introduction of such device for the profession and because of the considerably more complex effort needed for refinements as just described.

H. Metrology and Clinical Performance

Phase I. Development of Algorithms and Software for the Reduction of Data, Using the Weibull Distribution.

The software used for the processing of fracture data has been improved such that now the data, maximum likelihood estimates, and calculated cumulative probability curves can be exported to commercial graphics routines.

The Weibull distribution can be used to predict the characteristic lifetime of a given population even if only a few early failures have occurred. The process assumes a constant hazard rate and termination or censoring of the experiment at or near the last reported failure. This method has been applied to the bonding of fixed prostheses. The results have been submitted for publication. The shortcoming of this method (that all prostheses must be placed in service at the same time, as reported in NBSIR 89-4048) has been overcome and a complete description of the computer program and methods for use is given here as developed by Dr. Waldemar de Rijk just prior to his leaving his position with NIST.

"LIFETIME PREDICTIONS FROM CENSURED SETS USING THE WEIBULL DISTRIBUTION"

In 1939 Waloddi Weibull published an empirically derived distribution function to describe mechanical strength data.

The cumulative pdf (probability distribution function) is given by:

$$F(s) = 1 - \exp[-S/S_o)^m] \qquad \text{eqn. 1}$$

with $F(s)$ = cumulative probability of failure at stress S

S_o = Scale factor, or characteristic strength

m = Shape factor or Weibull modulus

The probability distribution function is given by:

$$f(x) = \left(\frac{m}{x_o}\right) \left(\frac{x}{x_o}\right)^{m-1} \exp\left[-\left(\frac{x}{x_o}\right)^m\right] \qquad \text{eqn. 2}$$

$$x > o \quad , x_o > o \quad , \quad m \geq 1$$

The major significance of this distribution over the Gaussian pdf is that the distribution reflects "real life" since:

1) Distribution is 0 at $x = 0$
2) Asymmetry is allowed (wear out)
3) The cumulative pdf is given in closed form

Having the distribution in closed form makes predictions possible when only a few data are available.

CENSORING

A group of data are considered censored when specimens have been removed from the study for a variety of reasons, not related to the test. There are several modes of censoring in life or reliability studies.

For the discussion here, the censoring is without replacement.

Type I. Simple Censoring (Censoring in Time)

A time to failure study of n samples is begun, with the decision made to terminate the experiment after t years.

Example: 20 amalgams are placed in a time to failure study which will be terminated after 5 years; the censoring is type I.

Type II. (Censoring According to Failure)

If a specific failure number is set as the terminating criterion then censoring is type II.

PROGRESSIVE CENSORING

Progressive censoring occurs when samples are removed from a population during a time-to-failure study.

COMPLETE SAMPLES

The estimates for m and t_o are obtained by a maximum likelihood estimate (MLE) routine. For n specimens with failure time: $t_1 \ldots t_i \ldots t_n$ the likelihood function is given by:

$$L(t_1 \ldots t_n, m, t_o) = \prod_{i=1}^{n} \left(\frac{m}{t_o}\right) \left(\frac{t_i}{t_o}\right)^{m-1} \exp\left[\frac{-t_i}{t_o} \right]^m \qquad \text{eqn. 3}$$

the maximum likelihood is found from:

$$\frac{\partial L}{\partial m} = 0 \qquad \text{eqn. 4}$$

and

$$\frac{\partial L}{\partial t_o} = 0 \qquad \text{eqn. 5}$$

If the 2 equations are solved and a substitution is made for t_o one finds:

$$\frac{1}{m} = \frac{\sum_{i=1}^{n} t_i^m \ln t_i}{\sum_{i=1}^{n} t_i^m} - \frac{1}{n} \sum_{i=1}^{n} \ln t_i \qquad \text{eqn. 6}$$

and

$$t_o = \left[\frac{1}{n} \sum_{i=1}^{n} t_i^m \right]^{1/m} \qquad \text{eqn. 7}$$

$$\text{eqn. 6a}$$

Note: $A(m) = \dfrac{\sum_{i}^{n} t_i^m \ln t_i}{\sum_{i}^{n} t_i^m} - \dfrac{i}{n} \sum_{i}^{n} \ln t_i$ is monotonically increasing with m; hence, A(m) = 1/m can be solved with iterative methods; Newton Raphson is frequently used.

Newton Raphson iteration:

$$\text{Let } F = \frac{\sum x_i{}^m \ln x_i}{\sum x_i{}^m} - \frac{1}{m} \sum \ln x_i \qquad \text{eqn. 8}$$

$$\text{and } F' = \frac{\partial F}{\partial m} \qquad \text{eqn. 9}$$

Let $\bar{m}$ be an initial estimate of m

Calculate F and F' then replace $\bar{m}$ with $\bar{\bar{m}}$

$$\bar{\bar{m}} = \bar{m} - \frac{F}{F'} \qquad \text{etc} \qquad \text{eqn. 10}$$

This iteration will find m quickly.
An example follows:
Conditions: a) All samples start at the same time; t_{in}.
b) There are n samples and r failures (hence n-r survivors) (Fig. 1).

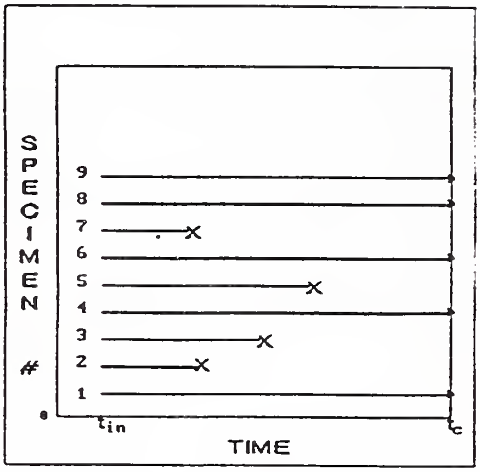

Fig. 1

Using the likelihood function we have:

$$\frac{1}{m} = \frac{\sum_{i=1}^{r} t_i{}^m \ln t_i + (n-r)\, t_c{}^m \ln t_c}{\sum^{r} t_i{}^m + (n-r)\, t_c{}^m} - \frac{1}{r} \sum_{i=1}^{r} \ln t_i \qquad (2)$$

where t_c is the censoring time. With iterative methods this can be solved for m.

A more <u>complex single censoring</u> occurs when not all specimens are "on line" at the same time ($t_{i_n} \neq$ constant). This is important in clinical cases where not all patients receive the treatment under investigation the same day.

We then have RUNOUT times or alive times as shown in Fig. 2.

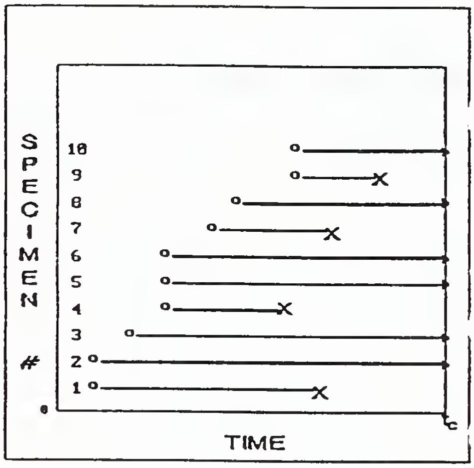

Fig. 2

The likelihood equation for this instance is: L ($\underline{t}$, t_o, m)

if $\underline{t} = (t_1, t_2 .. t_u, t_{k+1} ... t_n)$ eqn. 12

with t_1 the time for i = 1, 2 up to u failure times

and t_j the time for j = k + 1, ...n, runout times

then:

$$L = \prod^{u} \left(\frac{m}{t_o}\right) \left(\frac{t_i}{t_o}\right)^{m-1} \exp\ [-(t_i/t_o)^m \prod_{j=k+1}^{n} \exp\ [-\left(\frac{t_i}{t_o}\right)^m\ ] \qquad \text{eqn. 13}$$

(notation from Saunders, 1985)

When $\frac{\partial L}{\partial m} = 0$ and $\frac{\partial L}{\partial t_o} = 0$ eqn. 4 & 5

we find:

$$\frac{1}{m} = \frac{\sum_{i=1}^{n} t_i^{m} \ell n\, t_i}{\sum t_i^{m}} - \frac{1}{k} \sum_{i=1}^{n} \ell n\, t_i \qquad \text{eqn. 14}$$

An equation we have seen before as eqn. 6, which is special case of (14).

PROGRESSIVE CENSORING

A final adjustment can be made if we assume progressive censoring, as in Fig. 3.

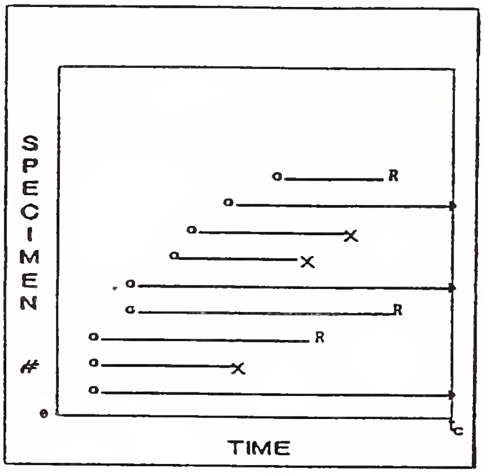

Fig. 3

o = start, t_{in}

R = remove from study

x = failure

→ = Runout

Since the solution for m and t_o involves only <u>actual</u> service times and <u>actual</u> runout times, the removed specimens Fig. 4a can be treated as runout times as shown in Figure 4b.

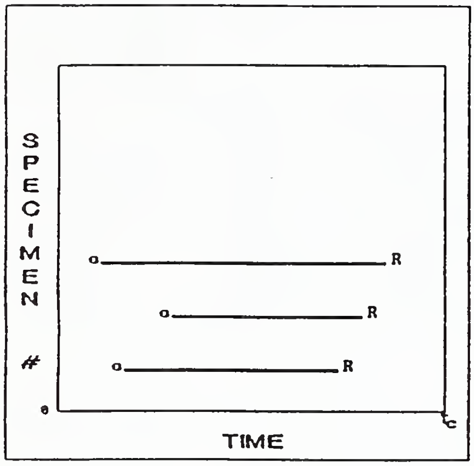

Fig. 4A

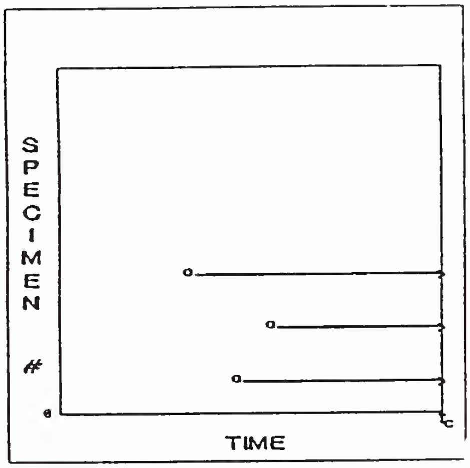

Fig. 4B

Hence for a population of n specimens we have n = k+r+s,

k = failures

r = runouts

s = removals

$$\frac{1}{m} = \frac{\sum_{i=1}^{n} t_i^m \ell n\ t_i}{\sum_{i=1}^{n} t_i^m} - \frac{1}{k}\sum_{i=1}^{k} \ell n\ t_i \tag{4}$$

Example

A set of lifetime data (in days) for a given product (Mann and Saunders 1985)

$\underline{92}$,	130,	233,	260,	320,
325,	$\underline{420}$,	430,	465,	518
640,	$\underline{700}$,	$\underline{710}$,	770,	830
1010,	$\underline{1020}$,	1280,	1330,	1690

for this set: $m = 1.62$

$t_o = 737.5$

Suppose the data underlined were removed from the set.

If we assume the remaining data represent 15 failures only and no accounting is made for having started with 20 samples (as is now common practice) then:

$m = 1.60 \quad t_o = 765.2.$

If we assume the five samples removed were removed in good standing then:

$m = 1.70 \quad t_o = 884.0$

If the 5 removed samples were *actual* runouts at 1800 days (5 years), then we would have had:

15 failures,

5 survivors

and the Weibull parameters would have been,

$m = 1.17 \quad t_o = 1274.0$

The above work shows how to use clinically available data to obtain a prediction of reliability, i.e. $R = 1-F(t)$ when censoring of various kinds are involved and the need to take advantage of the censored data to obtain the best estimates of R.

Phase II Analysis of Resin-Metal Bond Tests

This phase was first reported on in NBSIR 88-3782. The analysis of resin-metal tests has been extended to explore the effect of bond-layer thickness (50 and 200 μm) on the strength of a chemically bonded alloy system by using four point bending. The tensile bond strength between a Ni-Cr alloy and the resin based cement was calculated according to beam theory, and was analyzed by the Weibull method. Ultimately, the effectiveness of making comparisons between test results from different testing modes (such as bending and tensile) is what is to be determined. The hypothesis is that, by using the Weibull method of analysis with corrections for stress states and specimen sizes, tensile results from various test modes and/or laboratories might be brought into coincidence.

Specimens with 50 μm thickness of the cement produced a characteristic strength (S_o) of 110 MPa, a Weibull modulus (m) of 11.3, and a mean of 106 ± 10^* MPa. The specimen design is shown in Fig. 5, Weibull plots are shown in Fig. 6 and the results are shown in Table #1. Specimens with 200 μm thickness of the cement produced an S_o of 107 MPa, an m of 11.5 and a mean of 103 ± 10^* MPa. Specimens of the cement bulk (2 x 5 x 25 mm) tested by three-point bending produced an S_o of 85 MPa, an m of 6.8, and a mean of 80 ± 14^* MPa.

In Table #2 are shown the results of Table #1, corrected to a unit volume of material from the equivalent volumes shown, S_o's corrected to values for a unit volume were: 89 MPa, 98 MPa and 85 MPa for 50 μm, 200 μm and 2 x 5 x 25 mm specimens respectively. The corrected S_o of 200 μm specimens was higher than others ($p<0.05$). This suggests that either the failures of the cement-alloy system did not originate within the volume (cohesive failure) of the cement or that the assumption of a uniform stress (beam theory) throughout the bond layer is inappropriate and that beam theory is not proper for this application. Finite element stress analysis confirms the latter suggestion. The results do show that the fracture bending moment (a reliable, direct, comparative measure of the strength of the system) is not very sensitive to variation in thickness from 50 to 200 μm. This indicates that similar variations can be tolerated clinically.

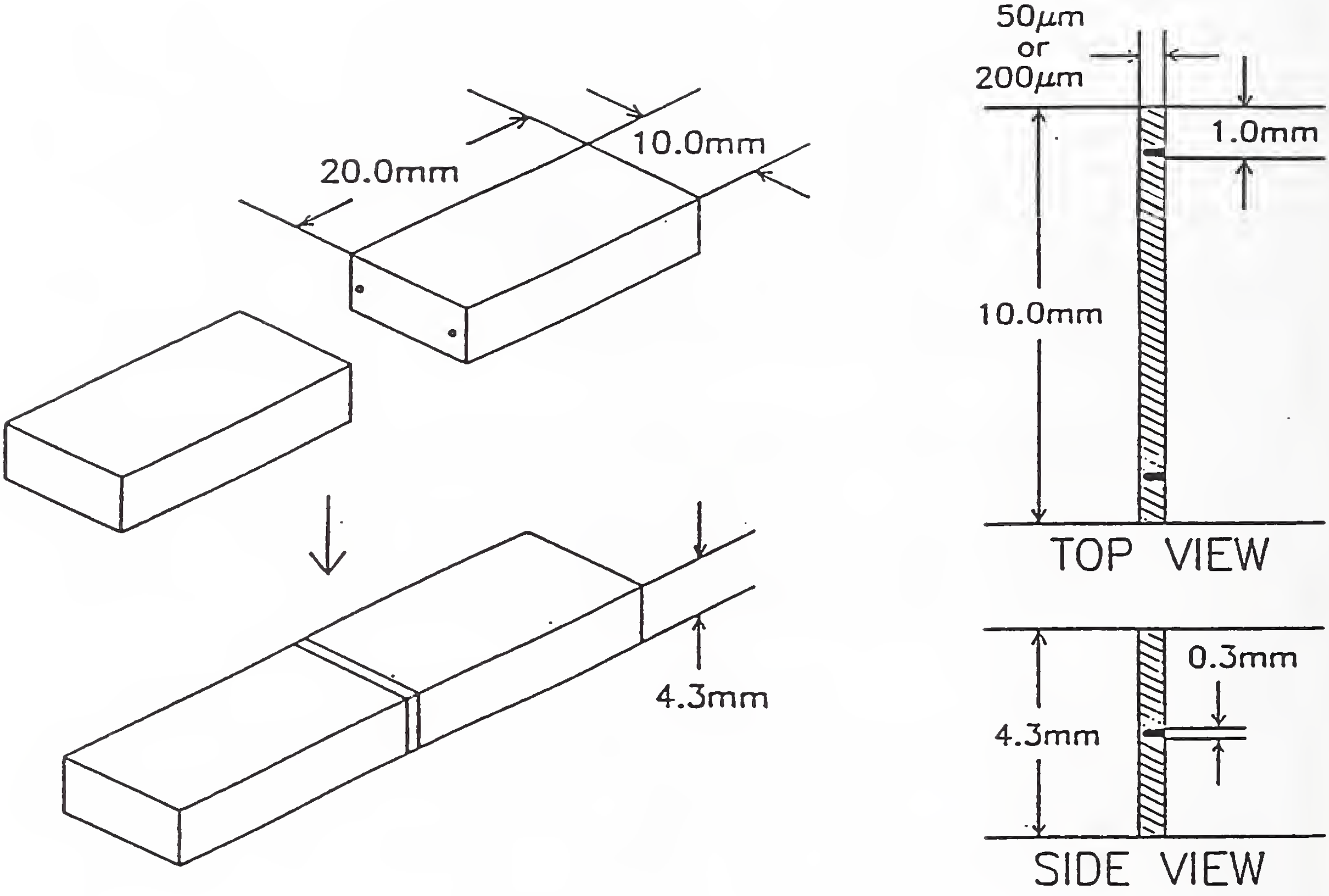

Fig. 5 - Test specimens consisted of a thin film of resin cement between two rectangular Ni-Cr casting slabs, one of which has 2 projections of 0.3 mm diameter and either 50 or 200 μm in height. These projections controlled the thickness of the cement layer.

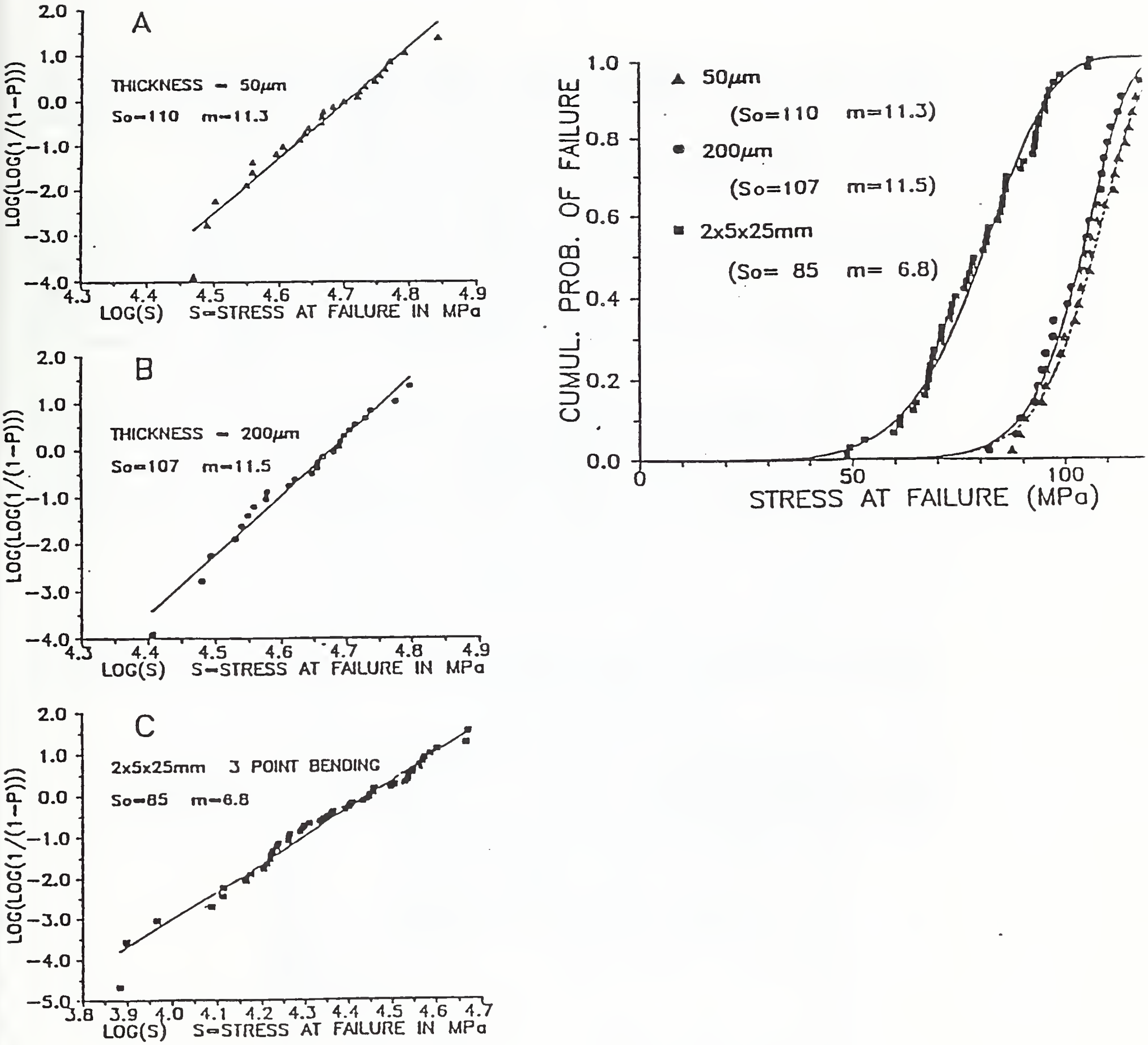

Fig. 6 - Plot of log(log(1/(1-P))) vs log(S) of 50 μm(A), 200 μm (B) and 2 x 5 x 24 mm(C) specimens. S_o and m were calculated by a least squares analysis. A plot of P vs S is shown for uses (A), (B), and (C),

The effect of the diameter of a projection (Fig. 5) on the local surface stress as calculated from beam theory is given in table #3. For a diameter of 0.3 mm (.07 of the total thickness) the surface stress is affected by less than two percent. A FEM showed an even smaller effect of the projections on the surface stress.

An elasticity FEM revealed large effects of material property differences on the surface stress distributed throughout the bond material region. There is a stress singularity at the metal-bond-layer interface and the stress distribution is as shown schematically in Fig. 7. The exact solution of this distribution is not yet available and will be attained when analytic singularity elements are introduced to the analysis.

In order to gain some insight into the magnitude of the effect of such a stress distribution on the measured strength of a bonding system, a stress profile similar to the FEM result was used for simulated risk-of-rupture calculations. The results are shown in Fig. 7 & 8. In Fig. 7 are shown three hypothetical surface stress distributions which were used to simulate the shape of the stress distribution obtained by FEM. These stress profiles were used to calculate the Weibull risk-of-rupture, B, where:

Table 3

The Effect of Projection Diameter on the Local Surface Stress in the Bonded Section of a Four-Point Bend Test Specimen and a ratio of Elastic Moduli (E_{metal}/E_{bond}) of 50.

Projection Diameter, Given As a Fraction of Total Thickness of the Slab	Surface Stress, Given as a Fraction of Surface Stress without Projections
.01	.9999
.02	.9996
.03	.9987
.04	.9969
.05	.9939
.06	.9895
.07	.9834
.08	.9753
.09	.9655
.10	.9533

$B = \int_{-X_o}^{+X_o} n(S)dx$ for a bond layer thickness of $2X_o$.

Here n(S) is assumed to follow the functional form which was empirically found by Weibull [4], ie. $n(S) = (S/S_o)^m$ where S is the stress at any surface, X; S_o is a characteristic strength and m is the Weibull modulus. For a uniform bending stress over a surface of a bond layer of width, $2X_o$, the risk-of-rupture, B_u, is ; $B_u = 2X_o \left(\frac{S}{S_{o,u}} \right)^m$.

For the same failure mode, the nonuniform stress distribution produces a different risk-of-rupture, B_n.

On the basis of the same average stress, S_a, the ratio of the characteristic strengths is

$\frac{S_{o,n}}{S_{o,u}} = \left(\frac{B_u}{B_n} \right)^{1/m}$. Ratios are shown in Fig. 8 for

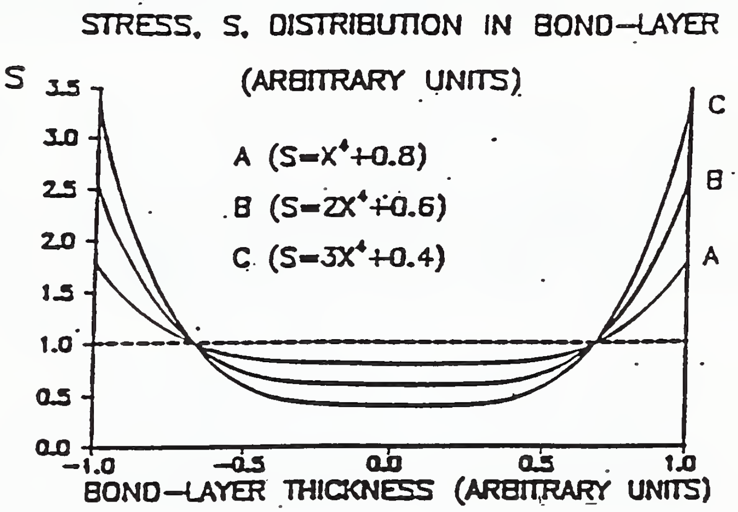

FIG. 7 THREE STRESS DISTRIBUTIONS EACH WITH THE SAME AVERAGE STRESS AS THE UNIFORM STRESS (DASHED LINE)

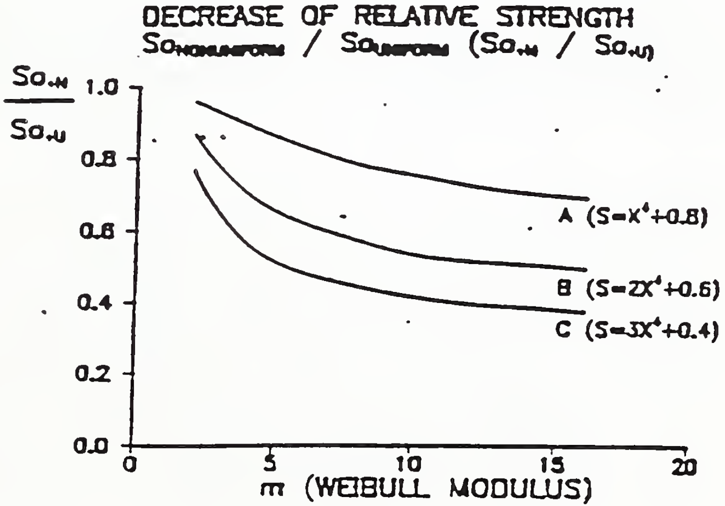

FIG. 8 DECREASE OF CHARACTERISTIC STRENGTH FOR THREE NONUNIFORM DISTRIBUTIONS

Table 1.

WEIBULL PARAMETERS AND MEAN STRENGTHS

Group	S_o (MPa) (range*)	m(range*)	N	Mean (SD)(MPa)
50 μm	110 (106-115)	11.3 (7.7-14.7)	25	106(10)
200 μm	107 (103-111)	11.5 (7.8-14.9)	25	103(10)
2x5x25mm	85 (81- 89)	6.8 (5.3- 8.2)	54	80(14)

*95% confidence range.

Table 2.

SIZE EFFECT CORRECTION OF S_o

Group	Volume (mm^3)	S_o (MPa) (range*)
50 μm	0.087	89 (85- 93)
200 μm	0.344	98 (94-102)
2x5x25mm	0.986	85 (81- 89)

*95% confidence range.

hypothetical stress distributions as functions of the Weibull modulus, m.

It is clear from these results that the probability of failure is higher for the same average stress if there is a nonuniform stress distribution. Therefore, if a nonuniform stress exists, but strengths are calculated on the assumption of a uniform stress, the bond-layer strength is <u>underestimated</u> because the overriding effects of higher than average stresses are underestimated.

Preliminary experiments using analysis by beam theory produced a range of strengths from 20 to 40 MPa, which is consistent with some results reported elsewhere [5]. The results of the analysis presented here indicates that these values would produce a characteristic strength which is low by ~ 20 to 60 percent.

In order to obtain a clearer concept of what the actual bond strengths are that can be attained in terms of stress, calculations of S_o should be made on the basis of the risk-of-rupture. This involves calculations of stress throughout the system. Furthermore, because there is an effect of specimen size (volume, area, etc.) on measured strengths, comparisons between laboratories must be made on the basis of unit or equivalent sizes after the risks of rupture have been calculated.

Multiple evaluations of S_o are necessary in order to make comparisons on the basis of either equivalent volumes, surfaces or edges etc. One advantage of such comparisons, using data from different sized test specimens within a laboratory is that the results can help to identify the origins of failures [6-7].

Phase III Analysis of Tensile Data from Composites Exposed to Food Simulating Fluids.

In light of previous findings [7] and the hypothesis put forth that the weighting factor for a mixed Weibull distribution, alpha, could be immersion-time dependent, an experiment was undertaken to determine the effect of immersion time on the Weibull parameters for a commercial dental composite.

The material for which previous data were obtained is no longer available. Therefore a different visible-light-initiated composite was used to determine if a mixed Weibull distribution was again observed after the composite had been exposed to a chemically active environment. In this study only ethanol was used as the food simulating liquid; however, the immersion time was taken to be the independent variable. The specific times of exposure were: 3 days, 3 weeks, 3 months and 6 months in 70% ethanol at 37°C. The results from diametral tensile tests were given in NBSIR 89-4048. In this case no evidence for a mixed Weibull distribution could be found for a more hydrophobic resin base (according to the manufacturer's indications).

Phase IV. Application of Diametral-Compression Testing of Dental Materials.

A investigation on the applicability of diametral-compression test (DCT) for dental materials is pursued in this study. The original assumptions of the Hertz formula and its history of application as used in diametral-compression testing are explored. The formula employed for calculating the uniform tensile stress, σ_x, normal to the diametral plane is

$$\sigma_x = \frac{2P}{\pi D \ell} \qquad (1)$$

where P, D and ℓ are the total loading, diameter, and length of specimen respectively. The load is assumed to be ideally concentrated as a line load.

This formula has been credited to Hertz [8]. Theoretical conditions under which the Hertz formula applies are 1) materials obey Hook's law and 2) the deformation is infinitesimal. In the theory of elasticity, concentrated load leads to a singularity with order of one ($\sigma_x \propto 1/r$ and $\sigma_y \propto 1/r$, Figure 2) at the loading points, i.e., stresses are infinite at these points ($r=0$).

Due to complex interactions at the contact surfaces between the platens of a testing machine and specimen, Figure 9, an unexpected failure phenomenon quite often occurs wherein the specimen fractures into more than the two equal pieces normally associated with tensile failure (Figure 10, single cleft fracture). Hertz based his work on the assumption that the deformation of the body is infinitesimal and loading is ideally concentrated. Theoretically, this concentrated load gives a stress singularity directly underneath the loading point and materials should fail in compression instead of tension due to this high stress localization. The uniform tensile stress along the diametral plane, Figure 11, obtained by the Hertz formula is only valid outside of the region affected by this singular point. In practice, no such point loads exist; the external loads must be spread into a finite region which is a surface of contact (Figure 12). If this contact surface is proportionally small compared to the diameter of specimen, the Hertz formula is still accurate enough for calculating the tensile stress along the diametral plane based on the slightly distributed loading. However, when the load is distributed over too small of a region, the failure of specimen can be caused either from localized compression or shear before the tension reaches it ultimate value along the diametral plane. Another possibility is that the specimen might elastically deform and at the same time develop complex stress fields due to coupling between application of the external load and the restraints imposed by the contact region. Failure also can be accompanied with excessive rather than limited deformation and this geometric nonlineality has to be included in the analysis. Sometimes materials fail in what appears to be tensile fracture, but at the onset of failure the original Hertz's assumption for the loading condition is severely violated and the Hertz formula, $\sigma_x=2P/\pi D\ell$, is not suitable for calculating the tensile stress on the diametral plan. Here, we often observe a double cleft fracture (DCF), Figure 13. A finite element analysis shows that such failure might be due to tensile stresses; however, the well known Hertz formula is not applicable to the DCF mode.

In order to more closely approximate the actual volumes of material involved in clinical practice, the size of specimens has been restricted to 6 mm in diameter and 3 mm in length. According to a previous study, the maximum valid padding width should be less than or equal to 0.6 mm ($b \leq 0.6mm$) for a specimen having this diameter if the equations (Eqs. 1 and 5-6) are used. With this small padding dimension, the simplicity of the diametral-compression test is destroyed, otherwise, the specimen may have undesired compressive/shear failure. Therefore another convenient, suitable testing method for obtaining a measure of the tensile strength of dental materials should be devised.

This will be an objective for continuation of this study. A manuscript entitled "Applicability of Diametral-Comparison Testing of Dental Materials" has been prepared for publication.

The width, "b" in Figure 4, of the rectangular contact area can be approximately given by (2):

$$b \simeq \sqrt{pDC} \qquad (2)$$

where $p = P/\ell$

$$\text{and } C = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_p^2}{E_p} \qquad (3)$$

where E_s, E_p and ν_s, ν_p are Young's moduli and Poisson ratios for specimen and platens respectively. Therefore, different types of platens can lead to different contact stress distributions. Figure 14 shows the effects of using platens with different stiffness. For hard platens, the stress will be higher at the edges of the contact area (Figure 14a); for soft platens, the stress will be higher at the center of the contact area (Figure 14b). Usually the platens are considered as rigid compared to the specimen; therefore, the stress distribution at the contact surface should have the general shape shown in Figure 14a.

There might be two cases of failure for which the Hertz formula cannot be used. They are:(i) if a very stiff material is tested (large magnitude of Young's modulus, E_s), the contact surface developed by the external load is very small before the specimen fails, and failure may occur from either the maximum compressive stresses developed directly under the loading area or from shear stresses. A local crushing due to compression or a fracture intersecting the diametral plane due to shear (Figure 15) should be observed in this case; (ii) if the material is flexible (small magnitude of Young's modulus, E_s), a greater amount of contact surface is developed by the external load before the specimen finally fails in tension. Yet the Hertz formula, Equation 1, is not applicable due to the loading condition being quite different from that originally assumed by Hertz. Since some dental adhesives have low elastic moduli (~4 Gpa), case (ii) might be observed in their testing if direct loading is applied. For higher modulus restorative materials (~16 Gpa), case (i) should usually be obtained if direct loading is applied. Tensile failures limited to the diametral plane with single cleft fractures, only occur for some materials in the direct loading condition, and even if they are, the real contact surface may not be within the range for which the Hertz formula is applicable.

We may conclude:

(1) The diametral-compression test as originally designed is oriented to have a desired tensile failure along the diametral plane of tested materials, and in conjunction with the Hertz formula, to evaluate the tensile strength of the materials.

(2) However, due to various types of material behavior and complex loading conditions imposed during the test, the failure mode might not be the same as that expected and the Hertz formula cannot be used to interpret these testing results. The fracture phenomenon should be fully analyzed, and validity of Hertz formula, Equation 1, fully understood, even if the failure is caused from tensile stresses. Any failure other than planar, single cleft fracture must be suspected as arising from stresses not calculable from the Hertz formula.

(3) The analysis presented is still only applicable for linear elastic materials with small deformations. Materials with lower stiffness may have larger deformations before failure; in this case the geometric nonlinearity must be considered. At present, no such analysis has been applied to take this into account. This will be the object of further investigation.

(4) The applicability of the equations (Eqs. 1 and 5-6) must be checked based on the deformations and observed fracture modes. The influence of material stiffness on the equations should be considered.

(5) Padding is highly recommended (this has been brought into attention for many years); however, its real significance has not been greatly appreciated in dental materials testing. The contact width of padding must be appropriately confined.

(6) An empirical study on the diametral-compression test should be more thoroughly investigated in order to have a complete comparison between the physical and mathematical models of the test.

(7) In order to more closely approximate the actual volumes of material involved in clinical practice, the size of specimens has been restricted to 6 mm in diameter and 3 mm in length. According to a

previous study, the maximum valid padding width should be less than or equal to 0.6 mm ($b \leq 0.6$mm) for a specimen having this diameter if the equations (Eqs. 1 and 5-6) are used. With this small padding dimension, the simplicity of the diametral-compression test is destroyed, otherwise, the specimen may have undesired compressive/shear failure. Therefore another convenient, suitable testing method for obtaining a measure of the tensile strength of dental materials should be devised.

This will be an objective for continuation of this study.

A manuscript entitled "Applicability of Diametral-Compression Testing of Dental Materials" has been prepared for publication.

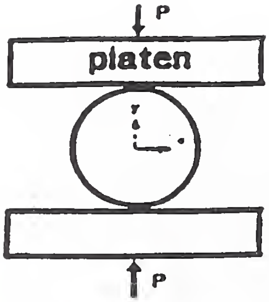

Fig. # 9a Diametral Compression Tes.

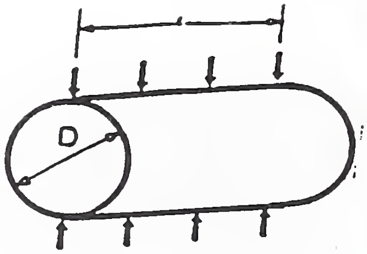

Fig. # 9b Test Specimen, Concentrated Loading.

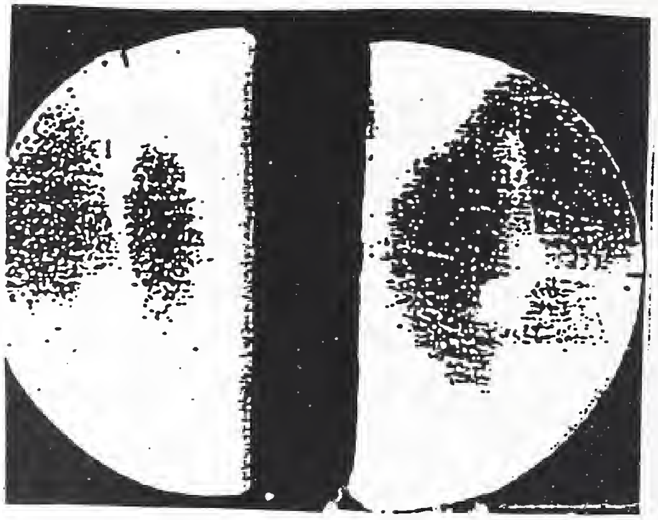

Fig. # 10 Single Cleft Fracture.

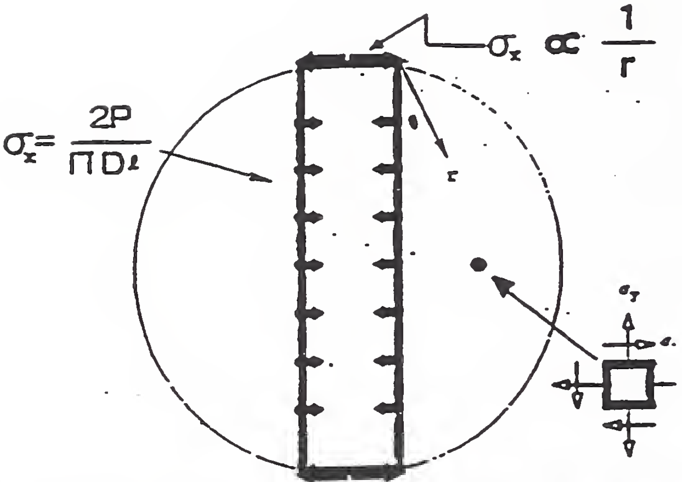

Fig. # 11 Tensile and Compressive Stresses Along Diametral Plane, Based on Hertz Formula (Requires Concentrated Loading.

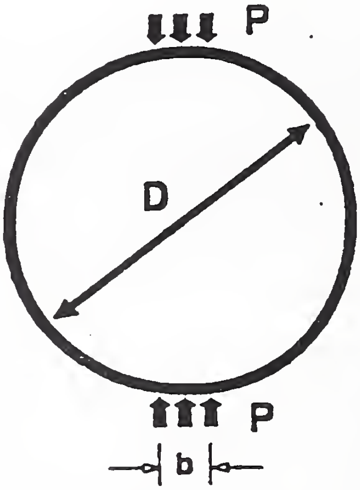

Fig. # 12 Nonconcentrated Loading Distribution Over Surface b.

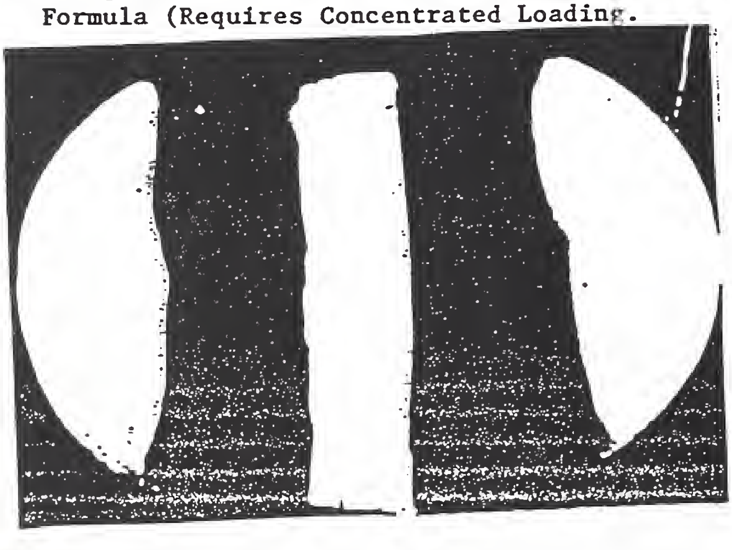

Fig. # 13 Double Cleft Fracture Hertz Formula Does Not Apply.

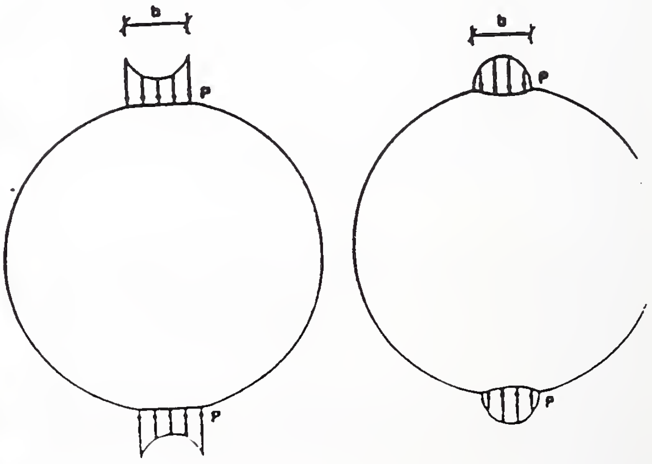

Fig. 14 Stress Distributions at Contact Surface Due to Hard and Soft Platens.

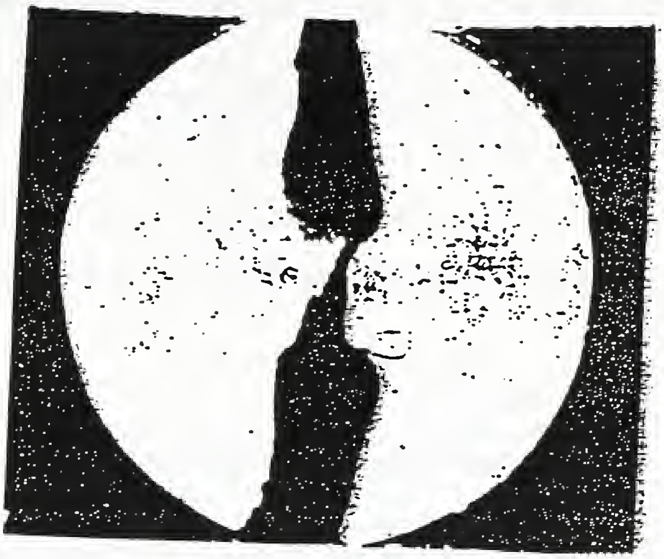

Fig. # 15 Shear Failure.

I. Metrology and Analysis: Stress in Dental Composites Bonded to Teeth

A mechanical engineer, Dr. Martin Chiang, has been added to the staff. Part of his responsibilities will included numerical analysis of tooth-composite systems. At the time of this writing, plans are being formulated for attacking this formidable problem.

The results from the study are expected to guide:

a) development of new cavity preparations.

b) clinical studies.

c) development of new materials.

d) development of restorative placement techniques.

At this time the computer systems, networking hookups and digitizing equipment have been installed. Studies are expected to commence within one year with the first phase aimed at developing an accurate three-dimensional model. Due to a concentration of efforts on other topics, especially modeling of mechanical test systems (bending, tension, diametral-tension) and a concerted effort on sterilization of dental instruments this work will receive less emphasis in 1990.

J. Metrology: Sterilization of Dental Instruments

PROGRESS REPORT

Accomplishments

Phase I. Development of Plasmas.

Numerous methods for igniting and controlling plasmas are being explored. A cooperative effort with the NIST Plasma Physics group has revealed effects which may be pertinent to microbial killing mechanisms. (See Phase II) At present, efforts are focussed on conducting kill kinetic studies under various conditions. One patent disclosure has been made in application for a patent.

Phase II. Effects of Plasma on Spores

Continuing Studies have shown that dental burs contaminated with b. subtilis from 10^6 colony forming units/mL-saline can be sterilized in static, sealed-off vacuum chambers and with up to 30 burs in contact. An abstract for presentation at the IADR meeting in March 1990 has been submitted.

Phase III. Effect of Plasmas on Materials

This phase has just been initiated.

Phase IV. Development of Suitable Biological Indicators for Controlled Sterilization Studies

This phase has just been initialed.

Phase V. Characterization of Plasmas

This phase has just been initialed

K. Metrology and Analysis: Dilatometer for Measuring Polymerization Shrinkage. (new task)

Background

Polymerization shrinkage is a continual problem for dental applications of polymeric materials. The shrinkage associated with the polymerization of the resin monomer to the crosslinked polymeric form imparts tensile mechanical stresses on the filling and cavity walls. Excessive shrinkage might lead to marginal leakage and possible failure of the filling. Attempts to reduce polymerization shrinkage have focused on new monomer formulations and the use of high content filler systems. Accurate, real-time measurements of polymerization shrinkage are important to follow the polymerization reaction kinetics and to assess the shrinkage characteristics of newly formulated resins and composites.

PROGRESS REPORT

Phase I. Volumetric Dilatometer Instrumentation.

Modifications of a polymerization shrinkage dilatometer [26] (also discussed in NBSIR 85-3119 and 86-3320) were completed for improved measurement precision, temperature stability and ease of specimen handling. This device continually measures the polymerization shrinkage of a photo-initiated composite sample placed on a glass slide by transmitting the volumetric changes through a column of mercury to a floating plunger attached to a linear variable differential transducer (LVDT). To improve measuring precision, the LVDT was recalibrated, rewired, and the plunger re-machined to increase the vibration isolation and decrease binding along the tube containing the mercury. Temperature stability is essential in this device because mercury has such a large thermal coefficient of expansion that any temperature fluctuations over the 24 hour test interval would introduce unacceptably large errors. By increasing insulation and modifying the air flow through the temperature controlled chamber we are able to decrease thermal drift (to less than +/- .02 degrees over 24 hours) and decrease the time needed for temperature stabilization after introduction of the test specimen (typically less than 5 minutes). This time interval is not a problem for visible-light activated polymers but is still too long for chemically activated polymers. The device has been shown to be sensitive to volume changes of +/- 10^{-5} cm^3. The limiting factor for precision seems to the measurement of the total volume (or density) of the polymerized sample which is determined in a liquid displacement pycnometer made from a ground glass joint with a long tapered opening to which the liquid is filled. Pycnometer measurements are made at a fixed temperature and volume and typically have an uncertainty of $+/-10^{-4}$ cm^3. The overall precision is estimated to be on the order of +/- 2% of the shrinkage values given. The accuracy of the device is difficult to assess, but shrinkage values for BIS-GMA resin and for a commercial dental composite agree well with those values reported in the literature.

Phase II. Assessment of Dilatometer Precision

A study was conducted using a BIS-GMA resin based composite (70 wt.% BIS-GMA, 30 wt.% TEGDMA) with varying filler contents to assess the accuracy and reproducibility of the polymerization shrinkage device. Composite samples were prepared with filler contents expressed as a percentage by weight up to a maximum working filler content of 83% for the macro filled samples, which corresponds to 67% by volume. Figure 16 shows the shrinkage values for the composite samples expressed as a function of the percent resin content by volume. Expressing the resin content by volume fraction is essential in order to obtain the expected linear relationship between the polymerization shrinkage and amount of resin present. The measured shrinkage for this unfilled BIS-GMA, TEGDMA resin was found to be 7.9% and decreased linearly as the volume percentage of the filler increases. The experimental data points followed the expected theoretical linear relationship up to the maximum filler content where the resin cannot completely wet the surface of the particulate filler. The slope of the linear fit is 7.8 with a correlation coefficient of 0.985.

Phase III. Future Studies

Further analysis of the data may be useful in determining the effective filler density and extent of air entrapment with different filler sizes and compositions. The modified dilatometer will allow accurate measurements of very low shrinkage or even expanding polymer composites under development in this laboratory. A new LVDT and power source have been purchased and modifications of the mercury U-tube are planed which should improve measurement resolution.

L. Profilometry (not active this period)

Work has not continued on this project as efforts were concentrated elsewhere. The computer and translational stages have been saved for future studies. The XT computer which is used to control the profilometer and collect data will be interfaced to the old wear machine which is currently being controlled by a very old cassette drive computer; see task K, preceding.

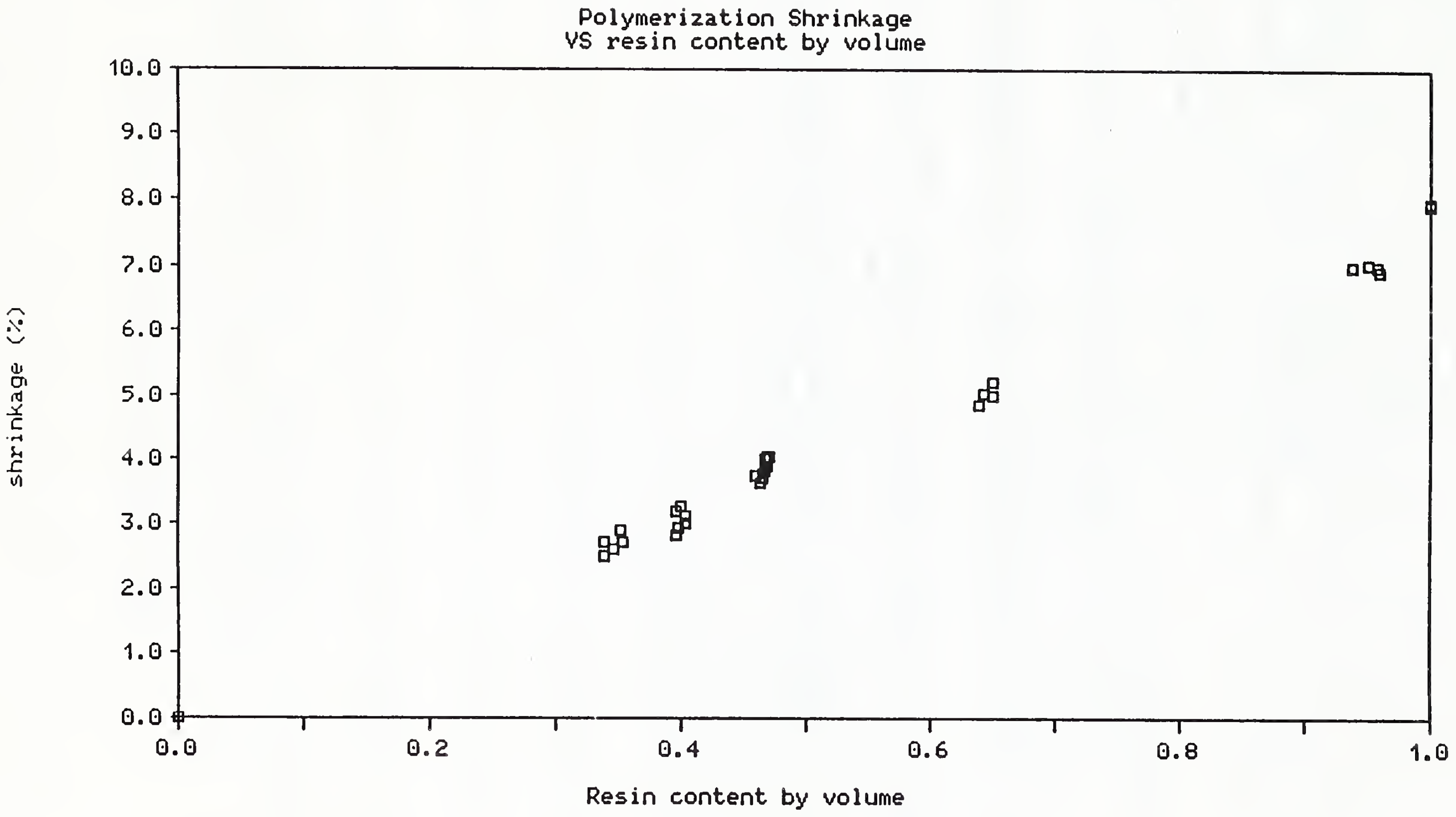
Polymerization Shrinkage
VS resin content by volume
shrinkage (%)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
Resin content by volume

Fig. 16

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Asaoka, K. and Tesk, J.A. Viscoelastic deformation of dental porcelain and porcelain-metal compatibility. To be submitted to Dental Mater.

Chiang, M.Y.M. and Tesk, J.A. Applicability of diametral-compression testing of dental materials. To be submitted to Dental Matls.

de Rijk, W.G., Tesk, J.A., Penn, R.W. and March, J. Applications of the Weibull method to statistical analysis of strength parameters of dental materials. Accepted for publication in Progress in Biomedical Polymers, Editors, Dunn, R. and Geberlein, G. Proceedings of a special symposium of the Am. Chem. Soc.

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Antonucci, J.M., Chairman, Gordon Research Conference on the "Science of Adhesion" August, 1990.

Tesk, J.A., Chairman, Conference on "Modern Instrumentation and Analysis Techniques" Oct 6-8, 1988. Co-Sponsored, National Institute of Standards and Technology and the Academy of Dental Materials.

de Rijk, W.G., Co-Chairman, Conference on "Modern Instrumentation and Analysis Techniques" Oct 6-8, 1988. Co-Sponsored, National Institute of Standards and Technology and the Academy of Dental Materials.

Tesk, J.A. Coordinator, Financial Affairs, Engineering Foundation Conference on "Performance of Dental Biomaterials Based on Engineering and Statistical Methods" August 13-18, 1989, Santa Barbara, California.

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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

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 used as well as 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 with laboratory test data. Metrology and analysis constitutes the underlying theme of investigations into porcelain-metal systems, casting of dental alloys and the expansion of dental casting investments.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

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