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Properties and Interactions of Oral Structures and Restorative Materials

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U.S. DEPARTMENT OF COMMERCE
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Annual Report for Period
October 1, 1986 to September 30, 1987

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Prepared for:

National Institute of Dental Research
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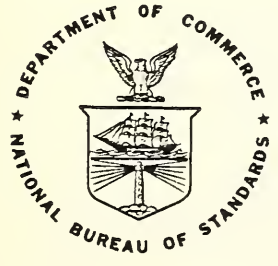

U.S. DEPARTMENT OF COMMERCE, C. William Verity, *Secretary*
NATIONAL BUREAUOF STANDARDS, Ernest Ambler, *Director*

CONTENTS

Section F - Antonucci

ABSTRACT

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

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

FY 87 SIGNIFICANT ACCOMPLISHMENTS

- Cellular and connective tissue reactions of hexyl vanillate cements approximate those of zinc oxide-eugenol (ZOE) cements.

- In animal studies intermediate restoratives based on hexyl vanillate elicit mild pulp reactions.

- Radiopaque denture resin containing pentabromophenyl methacrylate have acceptable characteristics, but working properties of this composition need improvement.

- A series of acrylic oligomers with pendant isocyanate groups have been synthesized and characterized.

- Oligomers with pendant isocyanate groups form stronger, more permanent, water resistant bonds to glutaraldehyde treated bone or soft tissues.

- Modified oligomers show great potential as dentin adhesives.

- Polyfluorinated resin-based composites were developed which have improved mechanical strength and wear resistance after exposure to oral fluids.

- Certain salts and complexes of amine polymerization activators were shown to be effective chemical and photochemical activators with fast-polymerizing resin systems.

- Some of the parameters contributing to the efficacy of visible light polymerization of dental resins and composites were identified resin-toughened glass ionomer cements can be used effectively in the composite-glass ionomer-dentin sandwich procedure without the use of prior etching and the use of bonding agents.

- The use of α-methylene γ-butyrolactone, a highly reactive analog of methylmethacrylate, resulted in dental resins with higher conversions.

- As a consequence of its high degree of cure and low solubility parameter value, the wear of a dual cured (chemical/visible-light activated) flexible-resin composite was essentially unaffected by previous storage in simulated intraoral solvents.

- A hybrid cement-composite comprised of a hybrid glass-ionomer cement and a "rubber toughening" organic polymer displayed far greater chemical resistance to organic acids and lacked the usual susceptibility to fracture displayed by conventional glass-ionomer cements.

- The surface stress σ of a porcelain slab, cooled at a constant cooling rate, q, was found by computer simulation to be represented by $\sigma = k\ell\ (q/q_o)^n$ where ℓ is the slab half-thickness; k and a are constants which depend on the material and q_o is a reference cooling rate.

- The coefficient of thermal expansion of dental porcelain, above the glass transition temperature, T_g, was found to strongly influence the residual stress in a porcelain slab (computer simulation).

- Castability studies have shown that batch-to-batch variations in investments can affect the castability value by 20% or more.

- Gas plasma ignition has been achieved for studies of plasma sterilization.

- Fracture followed by reglazing of a porcelain-metal composite slab was not found to result in significantly reduced system strength.

- The Weibull distribution was found to apply to failure data from resin-to-metal bond tests conducted at the U. of MD. The Gaussian distribution was incapable of describing the data.

- The strength of composite specimens aged in food-simulating liquids was found to be bimodally Weibull distributed. The weighting parameter (between modes) is suspected as being a time dependent factor.

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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 Restorations

Overview

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

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

Non-eugenol containing cements based on vanillate esters, o-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, and (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 exceed greatly 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

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

of their mechanical properties; (4) synthesis of cements containing the potentially caries-reducing syringic esters and evaluation of properties of the resulting cements; (5) modification of the cements by addition of small concentrations of additives such as acids, metals or fluorides to improve their properties and (6) 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. Two reviews stressing the commercial suitability of these cements for diverse applications have been prepared for publication.

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 two previous annual reports and references 9-14 and 16. These cements are being 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 connective tissue implantation technique (CTI) and the peritoneal cavity implantation technique (PCI), a promising method to quantitatively evaluate cellular response to implanted materials were employed. A mixed inflammatory cell response consisting of neutrophils, and macrophages occurred at most of the time periods for the cements in the CTI study. Similar cell populations, including lymphocytes, were observed with the PCI study. In histopathological observations each cement elicited a chronic foreign body reaction containing few chronic cells and mature fibroblastic activity. The intensity of the tissue reactions, for each cement, did not differ significantly with increasing time. The cellular and connective tissue reactions to HV approximated those of ZOE and ZP cements for both methodologies. These results demonstrated the acceptable biological performance of HV cement. The results have been written up and will be submitted to "Dental Materials" for publication.

(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.

Pulp reactions of two formulations of hexyl vanillate intermediate restorative when used with and without a protective base were reported by Kafrawy [17]. Both formulations were well tolerated by the dental pulp. When used with a protective base (Dycal), both compositions uniformly elicited mild reactions. Without a protective base, reactions generally were mild, however, some instances of moderate reactions were encountered. It would be of great

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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) a 150 Klux Xenon lamp, (2) a standard RS light source and (3) elevated temperature at 60°C, in air or water and under different experimental conditions for various time periods were investigated. Composites studied included chemically and light cured hybrid and microfilled resins and a material copolymerized by light and chemical aftercure. Color changes of composites intensified on increasing the irradiation time. Exposure to the two 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.

PROGRESS REPORT

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

Thermal exposure studies of the chemical or light cured, hybrid or microfilled composites were extended up to 34 months. Composites kept for this length of time at 37°C in the dark showed no color changes when compared to specimens kept at room temperature. Only the two chemically-cured commercial composites discolored at 60°C within 6 months in the dark. Even after 2 1/2 year storage at this temperature most of the visible light cured brands showed no or barely perceptible color changes. Most water-stored specimens discolored much more rapidly; some within one month and nearly all within 6 months. All materials gave perceptible or very perceptible color changes on 12 month storage in this

medium and further discoloration was observed after two 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.

Since the analytical high pressure liquid chromatograph identified only the major constituents of composite pastes, 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 infra-red or NMR. A manuscript summarizing these studies has been accepted for publication in Dental Materials. It includes comparison of our laboratory data with clinical studies of color changes of two of the chemically cured composites. The data indicate that these two restoratives, which pass the ANSI/ADA or ISO specification tests, cause discoloration in clinical use after two to three years.

Phase II. If Clinical Experience with Modern Composites is Favorable, then Formulate New Composites with Improved Color Stability and Aging Characteristics.

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

C. Development of Radiopaque Copolymeric Denture Resins

Overview

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

The state of the art of radiopaque plastics for dental applications has been reviewed [1,2].

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 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.

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.

To overcome the deficiencies encountered in the use of the brominated monomer, 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. These were sent to a manufacturer of denture resins. By using the procedure employed in the commercial synthesis, it is hoped that a suspension polymer powder of proper particle size is obtained to give the mix doughing and curing properties desirable for practical use. However 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 time. To prepare compositions with optimal clinically desirable properties, detailed studies of the effect of plasticizer and comonomers to increase swelling behavior of the powder will have to be conducted. 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 Formulations 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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D. Study of Adhesion and Adhesion Promoting Agents to Dentin

Overview

The main disadvantage of most dental restorative materials is the lack of adhesive bonding to tooth structures in the oral environment. These materials are kept in place solely by mechanical interlocking to the cavity preparation. A restorative that chemically bonds to tooth structure should inhibit the formation of secondary caries since it would prevent percolation of microorganisms and liquids by sealing the marginal areas of the restoration. With such a material, sealing of incipient carious lesions could be realized. An adhesive cement could lead to less invasive cavity preparations resulting in decreased loss of sound tooth substance. An effective bone adhesive to join polymer implants to bone as well as a soft tissue adhesive to bond denture resin or implants to this substrate also could find many applications in clinical dentistry.

Introduction

Many procedures to obtain permanent bonding to enamel or dentin have been suggested. Pretreatment of enamel with dilute acid enhances adhesion of restorative resins to enamel, but this is contraindicated for dentin. There are many constraints inherent in the long term bonding to dentin [1-4] and the present adhesives have found limited clinical use for this application. Surface grafting of monomers to mineralized tissues such as bone can be accomplished with persulfate [5] and to dentin with tri-*n*-butylborane oxide as initiator [6,7]. Zinc polyacrylates and glass ionomer cements adhere to enamel but only weakly to dentin. Excellent adhesion to dentin by acrylic resins is obtained with

isobutyl 2-cyanoacrylate, but the bond strength decreases on water exposure [8]. A mixture of a phosphorus ester of 2,2-bis[(p-hydroxy-3'-methacryloxypropoxy)phenyl] propane (BIS-GMA) and diluent monomer has been introduced commercially as a dentin-composite bonding agent [9]. Monomers with hydrophobic and hydrophilic moieties such as 4-methacryloxyethyl trimellitic anhydride (4-META) and the diadduct of hydroxyethyl methacrylate and pyromellitic anhydride (PMDM) bond dentin to acrylic resins [10,11]. Most effective are successive treatments of the dentin surface with oxalate, a 5 to 10 percent acetone solution of a glycine derivative (adduct of N-phenyl or N-p-tolylglycine and glycidyl methacrylate) followed by a 5 percent solution of PMDM in acetone [11]. Another good bonding agent to dentin is the mixture of 2-hydroxyethyl methacrylate and glutaraldehyde (Gluma) [12-19]. Thus, investigations during the last five years have developed luting agents that adequately bond to dentin. Major disadvantages of the presently recommended dentin bonding systems are (1) the tooth surface must undergo a number of pretreatments which are time-consuming and may limit the clinical usefulness and cost effectiveness of the process, (2) strict adherence to the protocol such as removal of excessive monomer and water from the treated tooth surface [11] are mandatory to obtain optimum bonding, and (3) the biocompatibility of the various reagents and compounds used in many of these tooth treatment procedures has not been fully explored.

The state of the art of soft tissue adhesives has been summarized by Manly [22] and Peppas and Buri [23].

Recently two difunctional monomers, 2-isocyanatoethyl methacrylate (IEM) and m-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI), i.e. compounds possessing polymerizable double bonds and reactive isocyanate groups, have been described in the literature [20,21]. These compounds react with reactive hydrogen groups such as the -OH, -SH or $-NH_2$ of the amino acids present in collagen, yielding covalent bonds with the tissue surface. The resulting adduct possesses vinyl groups that copolymerize in the presence of other vinyl groups to yield side chains grafted onto the collagenous tissues.

Objectives

Efforts are directed at developing film-forming surfaces that could serve as adhesives or sealants and synthesizing compounds and formulations containing functional groups that are effective adhesion promoters to mineralized tissues. Specifically these studies will (1) determine the grafting efficiency of oligomers and polymers of IEM or TMI and methacrylate and pendant isocyanate groups with the aim of obtaining a durable adhesive polymer coating on the dentin surface, (2) synthesize and evaluate the adhesive properties of methacrylate esters from a homocyclic tetracarboxylic dianhydride which is closely related to the

aromatic dianhydride used to prepare PMDM and (3) study the forces needed to fracture cemented surfaces and the relationship between retention of cemented crowns and the film thickness of the cement layer.

Accomplishments

Oligomers (low molecular weight polymers) were synthesized from 2-isocyanatoethyl methacrylate (IEM) and/or m-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI), two difunctional monomers (Fig. 1), and a number of simple methacrylates. The oligomers were characterized by their infra-red absorption spectra, refractive indices, and in some cases by gel permeation chromatography. The adhesive properties of the oligomers were evaluated by determining the tensile and shear strength of bone or dentin specimens cemented with these compounds. Permanent bond strength of the oligomers to bone was greater than that of other hard tissue adhesives. The oligomers also adhered well to dentin and soft tissues.

PROGRESS REPORT

Phase Ia. Synthesize and Characterize Oligomers with Pendant Isocyanate Groups.

A series of over 30 methacrylate oligomers containing pendant isocyanate groups were synthesized by reacting IEM and/or TMI in ethoxyethyl acetate with methacrylates ranging from methyl to stearyl methacrylates or alkyl-, cyclohexyl-, glycidyl i-bornyl-, or dicylopentenyloxyethyl methacrylate. Fig. 2 shows the structure of typical oligomers. Table 1 lists the oligomers synthesized, abbreviations used, ratio of monomeric reactants, state of the liquid and percentage of isocyanate per molecule. The oligomers are stable at room temperature. They were characterized by IR for -NCO, ester, C=C and aromatic groups, and by their refractive indices. They have a small number of residual double bonds and a molecular weight low enough so that the compounds are liquids at room temperature and dissolve readily in esters and chlorinated hydrocarbons. High pressure liquid chromatography (HPLC) showed no residual monomer. GPC and intrinsic viscosity (Table 2) of selected oligomers indicated a molecular weight range from 1400 to 2600. Isocyanate groups determined titrimetrically or spectrophotometrically ranged from 17.4% to 2.8% per molecule. The observed percentage of -NCO groups of most oligomers is considerably lower than the theoretical amount, i.e. the calculated value, assuming complete conversion of monomers to the oligomers. The higher molecular weight methacrylate esters are either more reactive than IEM or TMI or they sterically hinder the incorporation of the -NCO containing monomer into the oligomer chain. However, TMI is more reactive than low molecular weight

methacrylates such as methyl methacrylate (MMA) yielding oligomers containing a larger concentration of -NCO groups than would be expected.

Conversion of IEM or TMI to high boiling oligomers with low vapor pressure minimizes markedly the opportunity for skin contact with vapor and decreases greatly the rate of diffusion of the adhesive into the tissues. Since the adhesives described here comprise a generic series of oligomers having pendant isocyanate groups, it is possible to adjust many variables such as molecular weight, isocyanate content, volatility, viscosity, working properties and rate of diffusion of adhesive into tissues and to modify, if necessary, any adverse tissue reactions. Thus, in continuation of this work, oligomers in which the methacrylate groups have been replaced by vinyl groups such as IEM-vinyl acetate-TMI have been synthesized. Their adhesive properties are being evaluated.

A talk describing this synthesis has been presented. A manuscript summarizing this work is under editorial review.

Phase Ib. Prepare Adhesive Formulations and Evaluate Their Properties.

The tensile bond strengths of glutaraldehyde treated bovine bone cemented with over thirty oligomers (synthesized in phase Ia) are summarized in Table 3. The highest bond strengths were obtained with adhesive formulations of IEM (9.9 MPa) and TMI (9.0 MPa) followed by those containing IEM-butyl methacrylate (BMA)-TMI (8.3 MPa) or IEM-cyclohexyl methacrylate (CHMA) (8.4 MPa) with at least 9 other oligomer formulations fracturing above an applied load of 6 MPa. All specimens broke cohesively with many fracturing within the bone (Fig. 3). Bond strength was not reduced on thermocycling for 7 days between 5° and 55°C (540 cycles per day). Thus, exposure to water and thermal shock produced no deterioration of the bond as is experienced with isobutyl or other 2-cyanoacrylates [8]. To decrease the number of steps required for cementation, the glutaraldehyde pretreatment and application of the adhesive solution can be combined. The tensile strength of a joint cemented by this procedure was 5.5 MPa.

Substitution of other aldehydes for the glutaraldehyde was not successful. Pretreatment of the bone with either salicyl aldehyde or adipic dialdehyde and subsequent application of the oligomeric adhesive resulted in poor bonding.

Tensile bond strength of human dentin to composite was determined by the procedure of Kemper and Kilian [26] as modified by Lacefield et al [27] (Table 4). Bonds prepared

with IEM, IEM-dicyclopentenyloxyethyl methacrylate (QM) and IEM-glycidyl methacrylate (GMA)-TMI yielded maximum adhesion (5.93 MPa, 5.90 MPa and 5.03 MPa respectively) with four other adhesive formulations having bond strength values above 4.0 MPa, whereas Gluma (3.88 MPa) and N-toluyl glycine (NTG)-PMDM (3.12 MPa) yielded somewhat lower values. Bonding of bone to bone was always stronger than adhesion of dentin to composite as measured by the Kemper procedure. Except for IEM which adhered best with both substrates, the relative bond strength ranking of the other oligomeric adhesives varied greatly for the two substrates. The presence of additional functional groups in the methacrylate ester component of the oligomer such as glycidyl or alkyl groups improved adhesion to dentin whereas a cyclohexyl or long chain methacrylate enhanced adhesion to bone. Generally, adhesion measured by the Bowen test [28] which was used previously (see last annual report) gave considerably higher values than those obtained by the modified Kemper method. The former technique uses an appliance that establishes better contact between dentin and composite. Thus, by application of a load in the Bowen procedure, shrinkage of the composite on curing is directed laterally away from the dentin-composite interface and any loss of contact at the interface caused by polymerization shrinkage or the resulting stresses is minimized. The actual bond strength values recorded in the Kemper technique depend on the volume of resin cured in the specimen cup. Increasing the thickness of the composite disk cured in the cup from 1.0 mm to 3.0 mm, because of larger total curing shrinkage of the resin, decreased the measured bond strength. The results emphasize that adhesive strength measurements are greatly dependent on the test methods and experimental parameters employed. Tensile adhesive strength values are meaningful only if they are compared to some standard reference adhesive. Obviously, each procedure has an inherent bias, but any experimental bonding test should correlate as closely as possible with the actual conditions and results, a requirement which, because of many changing or unknown clinical conditions, is most difficult to fulfill.

All bond strength values of the human dentin-composite joint measured by both techniques were generally higher than those obtained with bovine dentin employing the Lee test [24] which is similar to the Kemper procedure. These higher bond strength values may be the result of (1) the more thorough preparation of the flattened human dentin surface compared to that employed for the bovine substrate, (2) the additional ethylenediaminetetra-acetic acid (EDTA) pretreatment for human dentin, or (3) the better contact at the tooth-adhesive and the adhesive-composite interface in the techniques employed for cementing human dentin to composite.

The following mechanism of adhesion of the oligomer to hard and soft tissues is postulated. Glutaraldehyde reacts with the $-NH_2$ groups of the collagenous surface. The resulting aminoalcohol and the isocyanate containing monomer yield a urethane containing double bonds. This urethane intermediate on polymerization adheres to methacrylate resin.

The oligomeric adhesives also bond well to soft tissue. Glutaraldehyde treated calfskin could be joined to calfskin or to denture base resin. Storage in air or water for 6 months did not destroy the integrity of the joint.

Conclusions

1. Monomers and low molecular weight (M.W.) liquid copolymers containing pendant isocyanate groups form stronger, more permanent, water-resistant bonds to glutaraldehyde treated bone than other adhesives.

2. The tensile adhesion of bovine or human dentin joined to composite restorative resins by these oligomers is similar to that of Gluma or PMDM dentin bonding agents.

3. The oligomeric adhesives form a permanent bond to soft tissues which is not destroyed by water.

One invited and two contributed talks were presented discussing these studies. A patent application has been filed for oligomeric adhesives with pendant isocyanate group.

Phase Ic. If Studies Conducted in Phase Ia and Ib are Successful, Initiate Cooperative Projects to Study Biocompatibility of These Adhesive Systems and Their Application in Dental Practice.

The biocompatibility of three oligomers furnished by this laboratory (TMI-SMA, IEM-BMA-TMI and IEM-CHMA-TMI) is being studied at Northwestern University, the Medical College of South Carolina and the Dental School, University of Regensburg, Germany. Over 300 bone specimens cemented with the three oligomers have been prepared and are being implanted by Dr. Kafrawy at the University of Indiana to study tissue reactions of the cured adhesive. The feasibility of using these materials as soft tissue adhesives is being explored at the Ohio State School of Dentistry.

Phase II. Synthesize the Dimethacrylate Ester of 5-(2,5-Dioxotetra-Hydrofuryl)-3-Methyl-3-Cyclohexene-1,2-Dicarboxylic Anhydride and Determine its Adhesion to Dentin.

Past Accomplishments

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

Phase III. Study the Effects of Film Thickness on the Retention of Cements.

Past Accomplishments

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

The effect of P/L ratio on FT or retention was more dependent on the composition of the brand than on the type of cement. For some polycarboxylate or ionomer cements, retention decreased with increasing film thickness. Little retention of well-fitted crowns was found for zinc phosphate powder-water mixes, although such retention had been suggested previously [25].

The P/L ratios suggested in the manufacturer's instructions did not always yield the maximum retention for either vented or unvented crowns. Venting of prepared crowns is indicated since this procedure usually increased their retention and produced smaller changes in film thickness on changing the P/L ratios. A paper describing this study has been published.

Table 1

OLIGOMERS SYNTHESIZED

Monomeric components: IEM, methacrylate ester and TMI[a]

Monomeric Components					% NCO		
IEM	Methacrylate Ester	TMI	Abbreviation	State of Liquid	Found Method 1[d]	Method 2[e]	Cal
IEM	Ethyl[b]		IEM-EA(1:1.5)	viscous	10.31	-	13
"	Butyl		IEM-BMA	"	-	9.35	14.
"	Stearyl		IEM-SMA	"	5.04	5.16	8.
"	Cyclohexyl		IEM-CHMA	"	-	-	12.
"	Dicyclopentenyloxyethyl		IEM-QM	"	5.68	4.66	10.
"	i-Bornyl		IEM-BOMA	"	-	-	-
	Butyl + Ethyl[b]		IEM-BMA-EA(1:1.3:1.8)	"	10.68	11.0	8.
	Methyl	TMI	TMI-MMA	fluid	15.83	17.01	13.
	Ethyl	"	TMI-EMA	viscous	-	8.81	13.
	Butyl	"	TMI-BMA	fluid	-	-	12.
	-	"	" " (1:1.4)	"	11.67	12.72	11.
	-	"	" " (1:2)	"	-	-	8.
	i-Butyl	"	TMI-iBMA	"	11.80	12.45	12.
	Hexyl	"	TMI-HMA	"	8.90	9.09	11.
	Lauryl	"	TMI-LMA	"	2.84	3.02	9.
	Stearyl	"	TMI-SMA	"	3.41	3.23	7.
	i-Bornyl	"	TMI-BOMA	viscous	-	5.63	9.
	Dicyclopentenyl-oxyethyl	"	TMI-QM	"	-	2.67	9.
	Dimethylaminoethyl	"	TMI-DMAEMA		-	-	11.
	Ethyl[b]	"	TMI-EA(1:2)	"	10.68	10.94	10.
IEM	-[b]	"	IEM-EA-TMI(1.3:1:1)	"	17.40	-	16.
"	Methyl	"	IEM-MMA-TMI	fluid	15.86	15.94	18.
"	Ethyl	"	IEM-EMA-TMI	"	16.31	-	17.
"	Butyl	"	IEM-BMA-TMI	"	16.16	15.92	16.
"	-	"	" " "(1.3:1.4:1)	viscous	15.55	13.47	13.
"	i-Butyl	"	IEM-iBMA-TMI	fluid	12.06	-	16.
"	Hexyl	"	IEM-HMA-TMI	"	14.50	14.63	15.
"	Lauryl	"	IEM-LMA-TMI	"	8.92	-	13.
"	Stearyl	"	IEM-SMA-TMI	"	5.17	5.12	12.
"	Allyl	"	IEM-AMA-TMI	viscous	14.80	15.12	17.
"	Cyclohexyl	"	IEM-CHMA-TMI	"	12.55	13.90	16.
"	Glycidyl	"	IEM-GMA-TMI	"	10.92	11.11	16.
"	i-Bornyl	"	IEM-BOMA-TMI	"	10.64	10.78	14.5
"	Dicylopentenyl-oxyethyl	"	IEM-QM-TMI	"	9.54	9.86	13.5

[a]Ratio of monomeric reactants is 1:1 or 1:1:1 respectively except were given in parentheses

[b]Ethyl acrylate

[c]Assuming complete conversion of momomers to oligomer

[d]by titration [e]spectrophotometrically

TABLE 2

INTRINSIC VISCOSITY OF OLIGOMERS AT 25°C

OLIGOMER	INTRINSIC VISCOSITY[a] dl/g
IEM-BMA	0.036
TMI-BMA	0.031
TMI-SMA	0.027
IEM-BMA-TMI	0.028
IEM-SMA-TMI	0.024
IEM-QM-TMI	0.030
IEM-CHMA-TMI	0.026

[a] Solvent: 1,2-dichloroethane

Based on $[\eta]_o = 17.0 \times 10^{-5} M_w^{0.68}$ (Billmeyer, J. Am. Chem Soc. 77, 4763 (1955) the molecular weight of these oligomers is estimated roughly between 2600 and 1400.

TABLE 3

TENSILE BOND STRENGTH OF BONE CEMENTED WITH VARIOUS ADHESIVES

Adhesive[a]	Bond Strength in MPa[b] after Storage in H_2O for 24 h. at 23°C	7 d. - thermocycled[c]
IEM	9.89 ± 1.44	7.41 ± 1.17
TMI	9.03 ± 1.79	8.38 ± 2.25
IEM-EA (1:1.5)	1.94 ± 0.76	-
" " (1:2)	2.50 ± 0.68	-
IEM-BMA	6.98 ± 1.97	-
IEM-SMA	1.23 ± 0.57	-
IEM-BOMA	2.76 ± 1.12	-
IEM-QM	5.23 ± 1.92	-
TMI - BMA (1:1.4)	7.94 ± 1.19	7.92 ± 2.21
TMI-BMA(1:1.4)-glutaraldehyde emulsion	5.46 ± 1.15	-
TMI-SMA	7.46 ± 1.15	8.66 ± 1.49
IEM-MMA-TMI	4.41 ± 1.53	-
IEM-EMA-TMI	6.15 ± 1.95	-
IEM-BMA-TMI(1.3:1.4:1)	8.25 ± 2.10[f]	7.47 ± 2.15
IEM-iBMA-TMI	6.61 ± 2.26	6.93 ± 1.34
IEM-HMA-TMI	3.53 ± 2.37	-
IEM-SMA-TMI	7.41 ± 1.52[g]	8.10 ± 1.80
IEM-CHMA-TMI	8.43 ± 2.65	8.19 ± 1.43
IEM-AMA-TMI	6.83 ± 2.32	6.73 ± 1.50
IEM-GMA-TMI	4.73 ± 1.99	-
IEM-BOMA-TMI	6.94 ± 2.71	7.24 ± 1.52
IEM-QM-TMI	7.53 ± 3.75	8.35 ± 1.53
Gluma[d]	7.25 ± 0.93	6.98 ± 0.93
Isobutyl cyanoacrylate	6.62 ± 1.73	4.52 ± 0.46[h]
Control[e]	1.07 ± 0.61	2.75 ± 0.31

[a] For abbrevations refer to Table 1.
[b] Mean of 10 specimens or those not fractured within the bone.
[c] 5°C and 55°C
[d] EDTA - glutaraldehyde - hydroxyethyl methacrylate
[e] Application of isocyanate containing adhesive was omitted.
[f] Mean of 28 specimens. [g] Mean of 16 specimens, [h] One day

Table 4

TENSILE BOND STRENGTH OF HUMAN DENTIN
CEMENTED TO COMPOSITE

Procedure as suggested by Kemper and modified by Lacefield et. al., J. Prosth. Dent. 53, 194, 1985.

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

Adhesive[a]	Bond Strength after 24 hr in H_2O
	MPa[b]
IEM	5.93 ± 2.23
TMI	4.02 ± 1.03
IEM-BMA	4.09 ± 1.58
IEM-BOMA	3.68 ± 1.34
IEM-QM	5.90 ± 2.80
TMI-BMA (1:1.4)	3.33 ± 1.03
TMI-SMA	3.61 ± 1.22
IEM-BMA-TMI (1.3:1.4:1)	3.61 ± 1.51
IEM-SMA-TMI	4.16 ± 2.19
IEM-AMA-TMI	4.58 ± 2.09
IEM-CHMA-TMI	2.15 ± 0.83
IEM-GMA-TMI	5.03 ± 2.47
IEM-BOMA-TMI	3.12 ± 2.47
IEM-QM-TMI	3.54 ± 1.19
Gluma	3.88 ± 2.48
NTG[c]-PMDM	3.12 ± 1.83

[a] For abbreviations refer to Table 1
[b] Mean of 5 specimens
[c] Ferric oxalate-N-tolylglycine-dimethacryloxyethylpyromellitic acid

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E. Monomers that Polymerize with Expansion

Introduction

Many researchers in the dental materials field view polymerization shrinkage as a necessary evil and attempt to design materials which minimize the problems associated with the contraction. However, the advent of double ring-opening polymerization has provided access to a new class of monomers capable of expansion in volume during polymerization. It is our expectation that incorporation of these new monomers in conventional resin formulations can limit polymerization shrinkage and its effects on adhesion, marginal integrity and other more subtle defects.

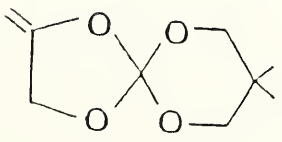
Objective

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

The recent focus of efforts in synthesis has been directed toward the preparation of spiro orthocarbonate monomers with reactivities that compare more favorably with those of methacrylates. Another concern has been to maximize ring-opening efficiency since addition polymerization through the double bond without ring-opening results in shrinkage. To this end, 2-methylene-8,8-dimethyl-1,4,6,10-tetraoxaspiro[4,5]decane (1) as well as the 2-methylene-8-spiro-(2'-norborn-5'-ene) (2) and 2,8-dimethylene (3) orthocarbonate derivatives were synthesized. The free radical polymerization of these monomers



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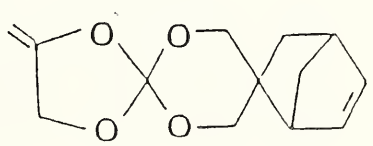

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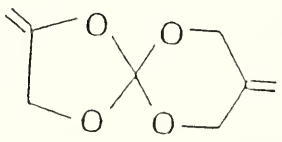


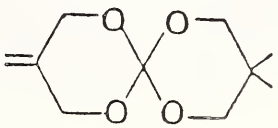
3

yields ring-opened polyketone-polycarbonates with small percentages of nonring-opened units depending on polymerization temperature. Monomer 1 was prepared as a relatively simple model of this class of compounds to investigate their polymerization behavior. The bulkier monomer 2 was designed to yield a higher modulus polymer that

should permit its incorporation into formulations in large percentages. The difunctional compound 3 was envisioned as cross-linkable monomer that would reduce the large degree o polymerization shrinkage normally associated with thi function.

Phase II. Polymerization

Homopolymers were obtained from monomers 1-3 as well as othe spiro orthocarbonate monomers previously synthesized. Thes were analyzed by nuclear magnetic resonance and infrare techniques to correlate the ring size and substitutio pattern of the monomer with the degree of ring-openin achieved during polymerization. The results showed tha placement of the polymerizable double bond on a five membere ring, and thereby adjacent to an oxygen, led to mor efficient ring-opening in comparison to monomers wit unsaturated six (4) or seven (5) membered spiro rings.



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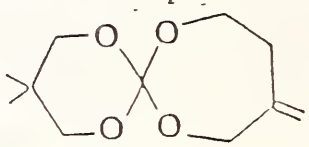


5

Also noted was the trend that higher degrees of substitutio in these monomers favored more ring-opening in the polymers This is presumably a result of steric hindrance or decrease mobility which inhibits the direct 1,2-additio polymerization pathway in favor of the ring-openin alternative. Monomer 3 was interesting in that at lo degrees of polymer conversion, a soluble ring-opened polyme with pendant double bonds was obtained. When driven to hig conversions, however, a cross-linked insoluble polymer wa formed.

A series of copolymers of spiro monomers 1,4 and 5 wit styrene was prepared to provide a comparison of the relativ reactivities associated with the various ring sizes. The reactivity of the five membered ring system in monomer 1 wa judged to be the greatest as evidenced by its higher degre of incorporation into the copolymer. Of monomers 4 and 5, which polymerize by a less energetically favorable mechanis than monomer 1, the seven membered ring appears to convey slightly more reactivity to the monomer than does the six membered ring. This can be explained by the additional rin strain that is relieved during the polymerization.

Phase III. Formulation

There were no formulation applications evaluated during this reporting period, however, the work with the new monomers described will be moving into this area shortly.

Phase IV. Evaluate the Properties of Polymer Formulated In Phase III

This work awaits developments from Phase III.

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

This work awaits completion of Phase IV.

References

[1] Thompson, V.P., Williams, E.F. and Bailey, W.J., Dental resins with reduced shrinkage during hardening, J. Dent. Res. 58, 1522-1532, (1979).

Contributed Talks

Stansbury, J.W. and Antonucci, J.M. Evaluation of α-methylene-γ-butyrolactone as a monomer in dental resin formulations. J. Dent. Res. 66 246, ABST No. 1116 (1987).

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) and in which water plays a role both in their setting and in the development of their molecular and micro structures, and (2) those that are relatively non-aqueous in nature, although catalytic amounts of water or other protic compounds (e.g., acetic acid) are needed to achieve clinically acceptable setting times (e.g., ZOE, EBA, HV-EBA, dimer acid, etc.)

This section is divided into four distinct parts:

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

I. Improvement of Dental Resin Systems for Composites and Sealants

Objective

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

PROGRESS REPORT

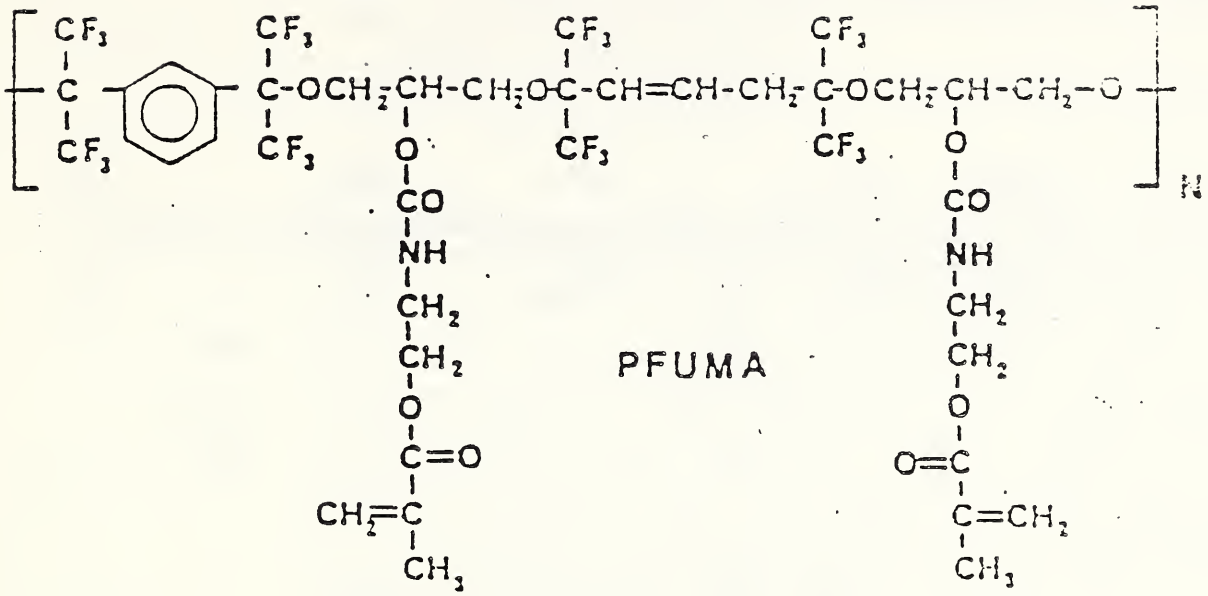
Phase I. Synthesis and Formulations

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

2,2,3,3,4,4,-hexafluoro-1,5-pentamethylene dimethacrylate, a highly fluorinated dimethacrylate of low viscosity suitable for use as a diluent monomer for PFUMA and PFMA (Figs. 1 & 2), was synthesized according to a previously described procedure [30]. This diluent monomer is derived from 1,5-hexafluoropentandiol and has a covalent fluorine content of 34%. The structure is shown below

$$CH_2=C(CH_3)CO_2CH_2CF_2CF_2CF_2CH_2O_2C(CH_3)C=CH_2$$

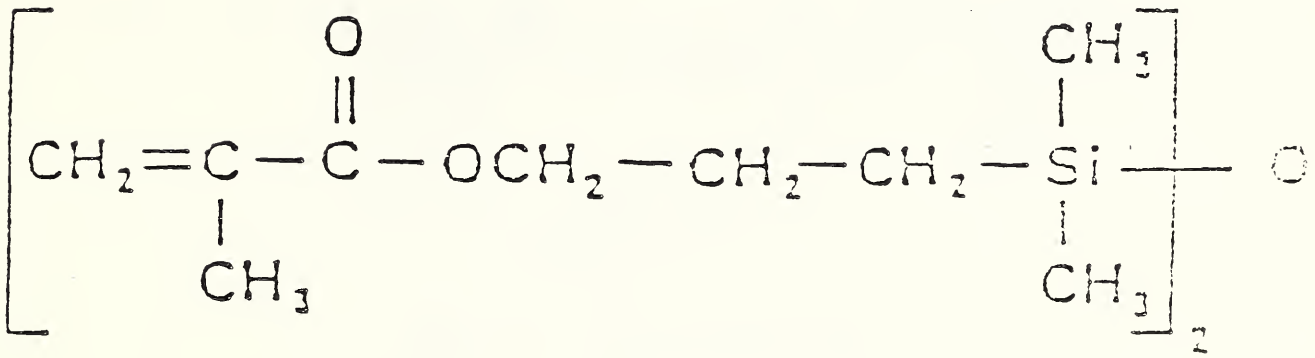
Figure 1



PFUMA

MW = 12,060

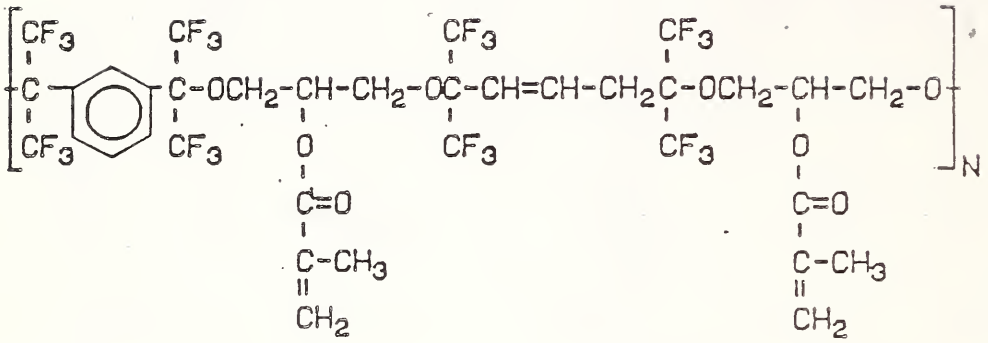
%F = 37.8



(BIS-MPTMS)

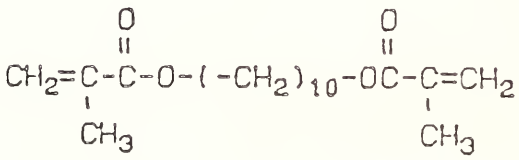
Structural formulas for (a) PFUMA and (b) BIS-MPTMS

STRUCTURE OF PFMA



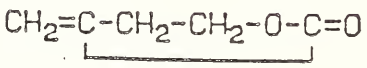
MW (Repeat) = 1032
Av. MW ≅ 10,320 (N ≅ 10)

STRUCTURE OF DMDMA



MW = 310

STRUCTURE OF α-MBL



MW = 98

Figure 2 Chemical structures of the base oligomer PFMA and the diluent monomers DMDMA and α-MBL

Thin layer chromatographic analysis revealed the presence of several impurities. Purification of this monomer is in progress. The purified diluent will be used to formulate more highly fluorinated resin systems than previously described.

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

Previously a visible light polymerizable composite formulation was prepared using the polyfluorinated prepolymer multifunctional urethane methacrylate, PFUMA, and bis(methacryloxypropyl) tetramethyldisiloxane (BIS-MPTMS, Fig. 1), a siloxane diluent monomer. A fine (2-4 μm) fused, silanized quartz powder was used as the reinforcing filler and camphorquinone, CQ, and ethyl 4-dimethylaminobenzoate, 4EDMAB, were used as the photoinitiator system (Table 1A). A second hydrophobic composite derived from the polyfluorinated prepolymer multifunctional methacrylate, PFMA, and decamethylene-1,10-dimethacrylate as the diluent, DMDMA (Fig. 2) was prepared using the same filler and photoinitiator systems (Table 1B). The wear properties of preconditioned specimens of these composites

Table 1A

COMPOSITION OF HYDROPHOBIC, FLEXIBLE
Resin-based COMPOSITES

Component			Weight Percent
PFUMA			22.03
BIS-MPTMS	-	Resin	9.44
CQ			0.05
4-EDMAB			0.22
Silanized Fused Quartz (2-4 μm)		Filler	68.26

showed a greater recovery and immunity from preconditioning treatments than conventional composites (see p. 69, Part II, section A).

PFMA resins with binary and ternary diluent monomer systems have been prepared such as shown in Tables 1C and 1D. The highly reactive monomer, α-MBL (see Fig. 2), was added to a PFMA/DMDMA resin and the concentration of the photoinitiator system increased slightly. Compared to composites from the formulation

given in Table 1B, composites derived from this resin formulation (Table 1C) were somewhat better cured and showed improved wear resistance. The use of the ternary diluent system with a dual cure initiator system (chemical/photochemical) is expected to further enhance the degree of cure and the depth of cure and lead to stronger, more durable composites (Table 1D). Preliminary results are in agreement with these expectations (see p. 79, Part II, section A). Composites prepared by the dual cure method had a higher diametral tensile strength (46 MPa) and degree of cure (65%) than the same composite formulation cured by visible light activation only (39 MPa, 53%).

Table 1B

Composition of the PFMA Composite

COMPONENT	WEIGHT PERCENT
Resin	
PFMA	21.700
DMDMA	9.052
4EDMAB	0.2015
CQ	0.0465
TOTAL	31.0*
Filler	
Silanized Fuzed Quartz (2-4μm)	69.0*

*Correspond to Matrix/Filler Ratio of 1/2.23 (wt/wt).

Table 1C

Composition of the α-MBL Modified PFMA Composite

COMPONENT	WEIGHT PERCENT
Resin	
PFMA	20.622
DMDMA	8.590
α-MBL	1.608
4EDMAB	0.218
CQ	0.062
TOTAL	31.1*
Silanized Fused Quartz (2-4μm)	68.9*

*Corresponds to Matrix/Filler Ratio of 1/2.22 (wt/wt)

Table 1D

Composition of Dual Cure PFMA Composite

COMPONENT	WEIGHT PERCENT
PFMA	21.64
MER[I]	5.70
DMDMA	3.17
α-MBL	0.43
4EDMAB	0.25
CQ	0.06
TOTAL RESIN	31.25*
SILANIZED FUSED QUARTZ (2-4μM) COATED WITH 1% b.w. BPO	68.75*

*Corresponds to matrix/filler ratio of 1/2.20
I bis(2-methacryloxyethyl)ether of resorcinol (32)

(c) Syntheses of highly fluorinated multifunctional methacrylates based on hexachlorocyclophosphazene [33,34]. This part of the project is deferred until a later period, depending on the outcome of (a) and (b).

(d) Silyl ether derivatives. Due to a concentration of efforts on other segments of the project, no work was done on this segment in FY87.

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

(f) Additives to improve the physical and chemical performance of resin-based materials by increasing the degree of polymerization and crosslink density.

Recently, α-methylene-γ-butyrolactone, α-MBL (see Figure 2), was investigated as a polymerizable monomer. Its structure can be envisioned as the cyclic analog of methyl methacrylate (MMA) but it is significantly more reactive than methacrylate monomers [1,2]. Polymers of α-MBL exhibit high glass transition temperatures (T_g) and show extreme solvent resistance [36,37]. In addition, due to its polar nature, α-MBL is an excellent diluent solvent for a variety of other monomers, oligomers and polymers. With its high reactivity in free radical polymerizations, α-MBL appeared to be a promising candidate for incorporation into dental resin formulations. It was reasoned that if the relatively low degree of cure that is common for conventional dental polymers could be significantly improved, then the interrelated properties of mechanical strength, chemical resistance and long term performance may also be favorably influenced.

An investigation was initiated to determine whether the incorporation of an α-methylene lactone comonomer into a conventional dental resin formulation could lead to an improvement in the mechanical properties and performance of these materials.

Synthesis:

α-Methylene-γ-butyrolactone (α-MBL) was selected for this evaluation due to its commercial availability and in light of a variety of properties that make its polymer appear particularly well suited for dental applications. A literature review of existing methods for the synthesis of α-methylene lactones was conducted and several particularly efficient techniques were noted for future utilization in the preparation of other members of this interesting class of monomers.

Formulation and Evaluation:

In preliminary work, 10 wt.% of α-MBL was added to a BIS-GMA/triethylene glycol dimethacrylate (TEGDMA) resin system resulting in a material with increased diametral

tensile and transverse strengths compared to the control. The degree of conversion for the α-MBL containing resins was also found to be significantly improved. These results can be attributed to the greater reactivity of the methylene lactone double bond compared to that of methacrylates in general and to the very rigid lactone ring structure appended to the polymer backbone. Because of the higher degrees of conversion, the improved solvent resistances and higher glass transition temperatures characteristic of polymers of α-MBL, dental materials with improved long term stabilities and wear properties should result. When higher percentages of α-MBL were incorporated in the resin formulation, a modest decline in physical properties was observed which appeared to indicate a segmented, nonrandom copolymer was being formed.

Since α-MBL has a boiling point about 100 degrees higher than MMA and also solvates poly(methylmethacrylate) and similar acrylate polymers and copolymers extremely well, it is under investigation as a replacement for MMA in denture bases, bone cements, and similar dental applications. This work was presented in part at the 1987 IADR meeting.

(g) Improved initiator systems for dental resins.

Visible light activated (VLA) composites polymerize by a light induced reaction involving a photooxidant, e.g., camphorquinone (CQ) and a photoreductant, e.g., a tertiary amine. This study was undertaken to determine some of the factors that may influence the degree of cure (DC), depth of cure (DOC), and degree of discoloration (DOD) of VLA resin-based dental materials. The parameters evaluated for their effect on these properties were (1) concentration of CQ, (2) type and concentration of tertiary amine, and (3) molar ratio of amine to CQ. For this study a commercial visible light source (Prismalite, Caulk/Dentsply) was used. DC was measured by FTIR methods [35,38-41]. DOC composite specimens were prepared by 10s irradiation from one side of composite filled steel cylindrical molds. After the uncured portion was removed, the hardened portion was measured by a micrometer. DOD was determined visually after 24 hours exposure to a S275 sunlamp.

Table 2

Acronyms, Names and Number of a Hydrogens of Amines

Acronyms	Name	No. of αH's
Aliphatic Amines		
MDEA	N-methyldiethanolamine (Aldrich Chemical Co.)	7
DMEB	2-(dimethylamino)ethyl benzoate (Quantacure DMA Ward & Blenkinsop)	8
I-907	2-methyl-1-[4-(methylthio)phenyl] 2-morpholinopropanone-1 (Irgacure 907, Ciba Geigy)	4
BPMPS	Bis(1,2,2,6,6-pentamethyl 1-4 piperidinyl) sebacate (Tinuvin 765, Ciba Geigy)	3
Aromatic Amines		
DMBA	(o, m, p) N,N-dimethylamino-benzoic acid (O, K&K Laboratories, Inc.; m and p, Aldrich Chemical Co)	6
DMB	para-dimethylamino-benzaldehyde (Aldrich Chemical Co.)	6
EDAB	Ethyl(o,m,p) N,N-dimethylamino-benzoate (o,p Aldrich Chemical Co. m, synthesized)	6
U8303	2-ethylhexyl-p-(dimethylamino)benzoate (Uvatone 8303, Upjohn Co.)	
BEA	2-n-Butoxyethyl-para-(dimethyl-amino) benzoate (Quantacure BEA, Ward & Blenkinsop)	6
DIPPT	N,N-Diisopropyl-p-toluidine (Ivoclar)	2
DtBDEA	3,5-Di-t-butyl-N,N-diethylaniline (Aldrich Chemical Co.)	4
BDMA	p-t-Butyl-N,N dimethylaniline (Aldrich Chemical Co.)	6
DMSX	Dimethylamino (sym) xylidene (N,N 3,5-Tetramethylaniline) (Aldrich Chemical Co.)	6
DMAϕS	Dimethylaminophenyl-trimethoxysilane (Petrarch Systems, Inc.)	6
DMABN	4-Dimethylaminobenzonitrile (Aldrich Chemical Co.)	6
DMAPE	4-Dimethylaminophenethanol (Aldrich Chemical Co.)	6
TPA	Triphenylamine (Eastman Kodak Co.)	0

Table 2 lists the names, acronyms and sources of the amines used in this study. The number of α-hydrogens for each amine is also given since according to current theories this may be a significant factor in the efficacy of the amine as a photoreductant for carbonyl oxidants, i.e. CQ [41]. The influence of chemical structure and concentration of the amine on DC of a commercial dental resin and the DOC of its composites is summarized in Table 3. Tables 4A-4E and Figures 3-5 illustrate how DC and DOC vary at constant amine concentrations and varying CQ concentrations and vice versa. Also shown is the effect of varying both the amine and CQ concentrations simultaneously (Table 4E). The amine used in these studies was 4EDMAB. A high correlation (r=0.95) was shown to exist between DC and DOC (Figure 6). Significantly, it was found that tertiary aromatic amines generally gave composites with higher DC's, DOC's and DOD's than tertiary aliphatic amines. Among tertiary aliphatic amines, DMEB, which has the most α-hydrogens (8), also gave resins with highest DC (68%). Surprisingly, the sterically hindered tertiary aliphatic amines, BPMPS, with only 3 α-hydrogens, and 1-907, with 4, had DC's of 65%. Of all the amines, BPMPS exhibited the lowest DOD (best color stability).

Among the tertiary aromatic amines, DC was highest for the esters of 4-DMAB, DMABN, DMSX, DMAØS, DMAPE and BDMA. DIPPT with only 2 α-hydrogens and TPA with no α-hydrogens gave resins with markedly lower DC's. Resins containing TPA required longer irradiation times (30s vs the usual 10s) to obtain coherent films. Even resins containing only CQ had a higher DC (63%) after 30s irradiation. Steric hindrance as well as the lack of sufficient α-hydrogens also may affect the photoreductive capacity of the amine. This is probably the reason ortho substituted amines (2-DMAB, 2-EDMAB) have lower DC's than their meta- and para-isomers. Of the aromatic amines studied DtBDEA gave resins and composites with the lowest DOD. This work was presented at the 1987 IADR meeting.

According to prevailing theories of amine activated chemical and photochemical initiation, the unshared electron pair of the tertiary amines is involved in complex formation with the oxidant prior to decomposition to initiating radicals [42,43]. Thus the "free" electrons of amine accelerators would be expected to play a critical role in both chemical and photochemical initiation mechanisms leading to the polymerization of resin-based materials. To test these theories a number of amine salts and complexes that tie up these "free" electrons of various tertiary amines were prepared and evaluated for their accelerative ability. It was expected, at least to some extent, that these types of amine derivatives would be less effective accelerators. Tables 5 and 6 list the acronyms names and structural formulas of some of the amines and coreactants used to prepare the amine salts or complexes. The acronyms, physical forms and idealized structures of these derivatives are given in Tables 7 and 8. In chemically

activated cures of viscous, crosslinking dental resin systems (e.g. BIS-GMA/TEGDMA, NCO[+]/TEGDMA) containing benzoyl peroxide (BPO), the amine salts and complexes derived from the more active tertiary aromatic amines (e.g. DMSX) were generally comparable in accelerative ability to their amine precursors and yielded fast setting, strong composites with excellent esthetics and color stabilities (Table 9). In addition, these types of amine derivatives are effective photoreductants for resins containing CQ and similar photooxidants. The conversions of vinyl groups in NCO/TEGDMA containing the various amines or their derivatives and 0.15 wt%. CQ after 10 seconds irradiation with a visible light source (Prismalite Caulk/Dentsply) are summarized in Table 10. The DOC's for a BIS-GMA/TEGDMA composite formulated with some of these amine derivatives are shown in Table 11. With slower polymerizing resin systems (e.g. methyl methacrylate), these types of amine derivatives are slower-acting as accelerators than their corresponding free amines. Also, in chemical cures utilizing BPO and fast polymerizing resins, derivatives of the slower-acting amine accelerators (e.g. 4-EDMAB) exhibit reduced accelerative potential. Dual curable resin systems based on some of these amine derivatives are under investigation. This work was presented at the 1987 IADR/AADR meeting.

[+]NCO is an oligomeric urethane derivative of BIS-GMA.

Table 3

Degree of Conversion (DC) of Resins† with Various Amines and Depth of Cure (DOC) of Composites made from these Resins and 75% Filler‡

Amine concentration (mmol%)	DC of Resin (%)	DOC of Composite (mm)
6.8 MDEA	62	4.30
4.1 DMEB	68	-
4.3 I 907	65	-
3.1 BPMPS	65	-
1.6 2-DMBA	52	4.60
1.6 3-DMBA	61	5.10
1.6 4-DMBA	64	5.40
3.4 DMB	67	5.50
4.1 2-EDAB	61	5.10
4.1 3-EDAB	65	5.30
4.1 4-EDAB	70	5.50
1.6 4-EDAB	70	5.50
4.2 BEA	71	-
4.2 U 8303	71	-
2.1 U 8303	70	-
4.2 DIPPT	57	-
4.2 DtBDEA	66	5.10
4.1 DMPT	67	-
2.0 BDMA	68	-
5.4 DMSX	70	-
2.0 DMSX	71	-
1.6 DMAϕS	69	-
4.1 DMABN	70	-
.8 DMAPE	67	5.50
1.6 DMAPE	68	5.60
4.1 DMAPE	70	5.40
3.1 TPA	54*	-
- -	63*	-

†Resin is a 1:1 mixture of an oligomeric urethane derivative of BIS-GMA, NCO, and TEGDMA (Caulk/Dentsply) containing 0.91 mmol% of CQ.
‡Silanized, radiopaque silica filler (average particle size 2μm)
*Values are for irradiation times of 30s instead of 10s.

Table 4

Depth of Cure of Composites (mm) and Degree of Conversion (%) of Resins with Varying Amine/CQ Concentrations. (Amine=4EDMAB).

(A) 1.6 mmol% Amine/Increasing CQ

Amine mmol%	CQ mmo%	DOC mm	Conversion %
1.6	.2	2.80	61
	.3	3.80	67
	.6	4.40	
	.9	5.00	71
	1.2	5.00	71
	1.5	4.90	
	1.8	5.40	
	2.1	5.50	75
	4.2	5.40	77

(B) 4.1 mmol% Amine/Increasing CQ

Amine mmol%	CQ mmol%	DOC mm	Conversion %
4.1	.2	3.70	
	.3	4.10	
	.6	4.70	
	.9	4.90	70
	1.2	5.20	
	1.5	5.60	
	1.8	5.50	
	2.1	5.50	
	4.2	5.30	

(C) 6.2 mmol% Amine/Increasing CQ

Amine mmol%	CQ mmo%	DOC mm	Conversion %
6.2	.2	3.80	61
	.3	4.40	67
	.6	4.70	71
	.9	5.10	72
	1.2	5.00	73
	1.5	5.20	73
	1.8	5.50	75
	2.1	5.40	76
	4.2	5.40	77

(D) Increasing Amine/.9 mmol% CQ

Amine mmol%	CQ mmol%	DOC mm	Conversion %
-	.9	2.90	44
.04		3.70	53
.4		4.70	63
.9		5.10	68
1.6		5.00	70
4.1		5.10	70
6.2		5.10	72

(E) Varying Ratios of Amine and CQ

Amine mmol%	CQ mmol %	Amine/CQ molar ratio	Conversion %
.4	.9	0.44	63
.9	.9	1	68
1.8	.9	2	70
4.1	.9	4.6	70
6.2	.9	6.9	72
.4	.9	0.44	63
.9	1.8	0.50	71
1.8	4.2	0.43	77

TABLE 5

AMINES

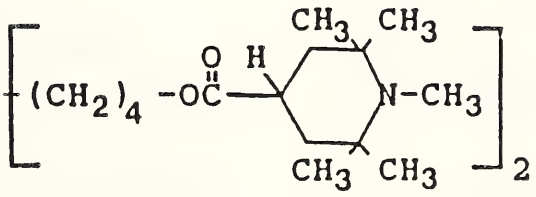
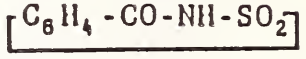
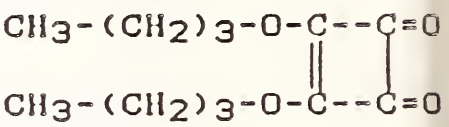
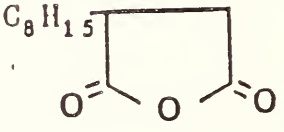
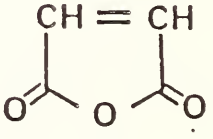
ACRONYM	NAME	STRUCTURE
DMSX	N,N-DIMETHYL-SYM-XYLIDENE	$3,5\text{-}(CH_3)_2(C_6H_3N(CH_3)_2$
DMAPE	4-N,N-DIMETHYLAMINOPHENETHANOL	$4\text{-}HOCH_2CH_2C_6H_4N(CH_3)_2$
DtBDEA	N-N-DIETHYL-3,5-DI-T-BUTYLANILINE	$3,5[(CH_3)_3\text{-}C\text{-}]_2C_6H_3N(CH_2CH_3)_2$
4EDMAB	ETHYL 4-N,N-DIMETHYLAMINOBENZOATE	$4\text{-}CH_3CH_2O_2C\text{-}C_6H_4N(CH_3)_2$
4DMABN	4-N,N-DIMETHYLAMINOBENZONITRILE	$4\text{-}NCC_6H_4N(CH_3)_2$
DMB	4-N,N-DIMETHYLAMINOBENZALDEHYDE	$4\text{-}OCHC_6H_4N(CH_3)_2$
BPMPS	BIS(1,2,2,6-PENTAMETHYL-1,4-PIPERIDINYL)SEBACATE (TINUVIN 765)	

TABLE 6

REACTANTS USED TO PREPARE AMINE SALTS OR COMPLEXES

ACRONYM	NAME	STRUCTURE
OXA	OXALIC ACID	$HO_2C\text{-}CO_2H$
PYA	PYRUVIC ACID	CH_3COCO_2H
MPY	METHYL PYRUVATE	$CH_3COCO_2CH_3$
PGA	PHENYLGLYOXYLIC ACID	$C_6H_4COCO_2H$
EPG	ETHYL PHENYLGLYOXYLATE	$C_6H_4COCO_2CH_2CH_3$
TFAA	TRIFLUOROACETIC ACID	CF_3CO_2H
PFOA	PERFLUOROOCTANOIC ACID	$CF_3(CF_2)_6CO_2H$
PFBA	PENTAFLUOROBENZOIC ACID	$C_6F_5CO_2H$
PTSA	P-TOLUENE SULFONIC ACID	$P\text{-}CH_3C_6H_4SO_3H$
PTsA	P-TOLUENE SULFINIC ACID	$P\text{-}CH_3C_6H_4SO_2H$
SAC	O-BENZOIC SULFIMIDE (SACCHARIN)	
BBSQ	3,4-DIBUTYL SQUARATE	

ANHYDRIDES

PHA	PHTHALIC ANHYDRIDE	$1,2C_6H_4(CO)_2O$
CHA	CYCLOHEXANE-1,2-ANHYDRIDE	$1,2\text{-}C_6H_{10}(CO)_2O$
BTDA	3,3,'4,4'BENZOPHENONE TETRACARBOXYLIC DIANHYDRIDE	$O(OC)_2\text{-}C_6H_3COC_6H_3(CO)_2($
OSA	OCTENYLSUCCINIC ANHYDRIDE	
MA	MALEIC ANHYDRIDE	

HALIDES

BZC	BENZYL CHLORIDE	$C_6H_5CH_2CL$
α-CAP	α-CHLOROACETOPHENONE	$C_6H_5COCH_2CL$

TABLE 7

Physical Form of

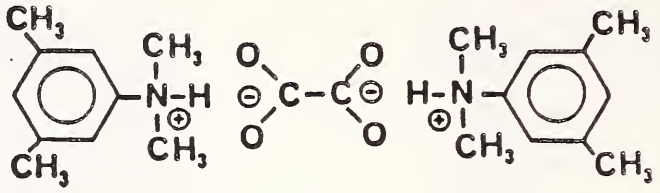
Some Amine Salts and Complexes

ACID	AMINE	SALT	PHYSICAL FORM
OXA	4EDMAB	DOXA-4EDMAB	WHITE SOLID
OXA	DMABN	DOXA-DMABN	" "
OXA	DMB	DOXA-DMB	PALE YEL. SOLID
OXA	DMSX	DOXA-DMSX	WHITE SOLID
OXA	DtBDEA	DOXA-DtBDEA	" "
OXA	DMAPE	DOXA-DMAPE	OFF WHITE SOLID
PYA	4EDMAB	PYA-4EDMAB	PALE YEL. SOLID
PYA	DMAPE	PYA-DMAPE	VIS., YEL. LIQUID
PYA	DMSX	PYA-DMSX	" " "
TFAA	DMSX	TFAA-DMSX	YEL. VIS. LIQ→ SOLID→BROWN VIS., LIQUID
PFOA	DMSX	PFOA-DMSX	VIS.,LIGHT BROWN LIQUID
PFOA	4EDMAB	PFOA-4EDMAB	VERY VIS. ORANGE LIQUID
PFBA	DMSX	PFBA-DMSX	BROWN SOLID
BF_3	DMSX	BF_3-DMSX	WHITE SOLID
PTSA	DMSX	PTSA-DMSX	" "
PTSA	4EDMAB	PTSA-4EDMAB	" "
PTsA	DMSX	PTsA-DMSX	VIS, BROWN LIQUID
PTsA	4EDMAB	PTsA-4EDMAB	VIS, RED LIQUID
SAC	DMSX	SAC-DMSX	LIGHT, TAN SOLID
PTSA	BPMPS	PTSA-BPMPS	VERY VIS, SLIGHTLY OPAQUE LIQUID
OSA	DMSX	OSA-DMSX	PALE RED LIQUID
OSA	4EDMAB	OSA-4EDMAB	VIS, YEL LIQUID
BTDA	DMSX	BTDA-DMSX	PALE, YEL SOLID
MPY	DMSX	MPY-DMSX	YEL. LIQUID
BZC	DMSX	BZC-DMSX	WHITE SOLID
α-CAP	DMSX	α-CAP-DMSX	YEL. SOLID

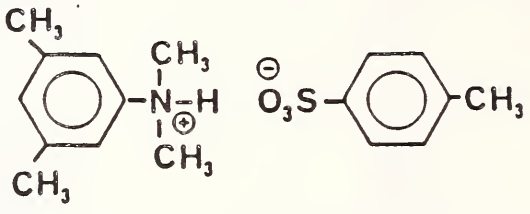
IDEALIZED STRUCTURES OF SALTS OF TERTIARY AMINES

Carboxylic-Amine Salts

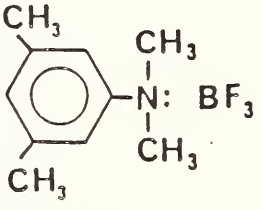
ketocarboxylic; polyfluorocarboxylic, dicarboxylic;



Sulfonates, Sulfinates, Saccharinates



Lewis Acid Complexes



Other Complexes of Tertiary Amines

Esters; Anhydrides

ESTER or ANHYDRIDE + AMINE $\rightleftharpoons$ COMPLEX

usually colored

Quarternary Salts of Amines

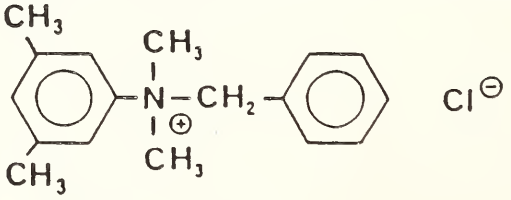


TABLE 9

Setting times of Chemically-Activated Composites* Using Amine Salts or Complexes Accelerators at 37°C

Accelerator	(Conc in Resin) (wt %)	Equivalent amine Conc (wt)%	Setting Time (MIN)
DOXA-DMSX	0.093	0.07	1.75
PTSA-DMSX	0.14	0.06	1.8
PTsA-DMSX	0.11	0.05	2.5
" "	0.32	0.16	1.5
PFOA-DMSX	0.47	0.12	1.5
PFBA-DMSX	0.40	0.17	1.1
BF_3-DMSX	0.082	0.057	1.75
SAC-DMSX	0.12	0.055	1.5
OSA-DMSX	0.10	0.04	2.5
" "	0.20	0.08	1.25
BTDA-DMSX	0.10	0.048	3.0
BZC-DMSX	0.24	0.13	>1HOUR
ABOVE SOLUTION OF RESIN HEATED AT 60°C FOR 30 M			~20M+
α-CAP-DMSX	0.16	0.078	1.75
DMSX	0.055	0.055	2.0
"	0.11 CONTROLS	0.11	1.0

*Composites were prepared by mixing at room temperature 4 parts b. w. of 1% BPO, silanized glass with 1 part b.w. of activated BIS-GMA/TEGDMA (7/3). The mixing time at room temperature was 40-45 seconds.
+Presumably the quaternary salt BZC-DMSX is decomposing into BZC and DMSX on heating. (Otsu et al, 1969)

TABLE 10

Degree of cure (Conversion) of Vinyl Groups in NCO Resin*
Using Amine Salts and Complexes

Photoaccelerator	(conc wt%)	Equivalent Free Amine (conc wt %)	Percent Conversion
PYA-DMAPE	1.0	0.68	63
DMAPE	0.15	0.15	68
DOXA-DMB	0.55	0.30	64
DMB	0.50	0.50	67
PYA-DMABN	1.0	0.62	67
MPY-DMABN	1.02	0.60	69
DBSQ-DMABN (2:1)	1.06	0.30	68
" " "	2.46	0.60	70
DMABN		0.60	70
TFAA-DMSX	0.53	0.30	66
DMSX	0.30	0.30	71
PYA-4EDMAB	1.0	0.80	68
MPY-4EDMAB	1.22	0.80	69
4EDMAB	0.80	0.80	70
2-DMBA	0.26	?	52
3-DMBA	0.26	?	61
4-DMBA	0.26	?	64
NONE	-	-	44

*Concentration CQ = 0.15% b.w.; time of irradiation =10 seconds

TABLE 11

Depth of Cure Visible-Light Activated Composites
Using Amine Salts and Complexes*

Photoaccelerator	Conc (wt%)	Equivalant Amine (Conc (wt%)	DOC (mm)
DtBDEA	0.54	0.54	6.0
DOXA-DtBDEA	0.64	0.54	7.6
4EDMAB	0.70	0.70	8.1
PGA (1%)+4EDMAB	-	0.70	8.6
OSA-4EDMAB	1.0	0.47	8.7

*DOC were determined using 10 mm deep stainless steel molds. Composite pastes, consisting of 4 parts of silanized radiopaque glass (average size =45μm) and 1 part of activated BIS-GMA/TEGDMA (7/3) containing 0.15% b.w. CQ and the above photoaccelerators, were packed in the mold and the ends covered with strips of mylar film. Irradiation time, for sets of 3 specimens for each formulation, was 10 seconds. The uncured portion was removed with a plastic spatula and the hardened cylinder measured for DOC with a micrometer.

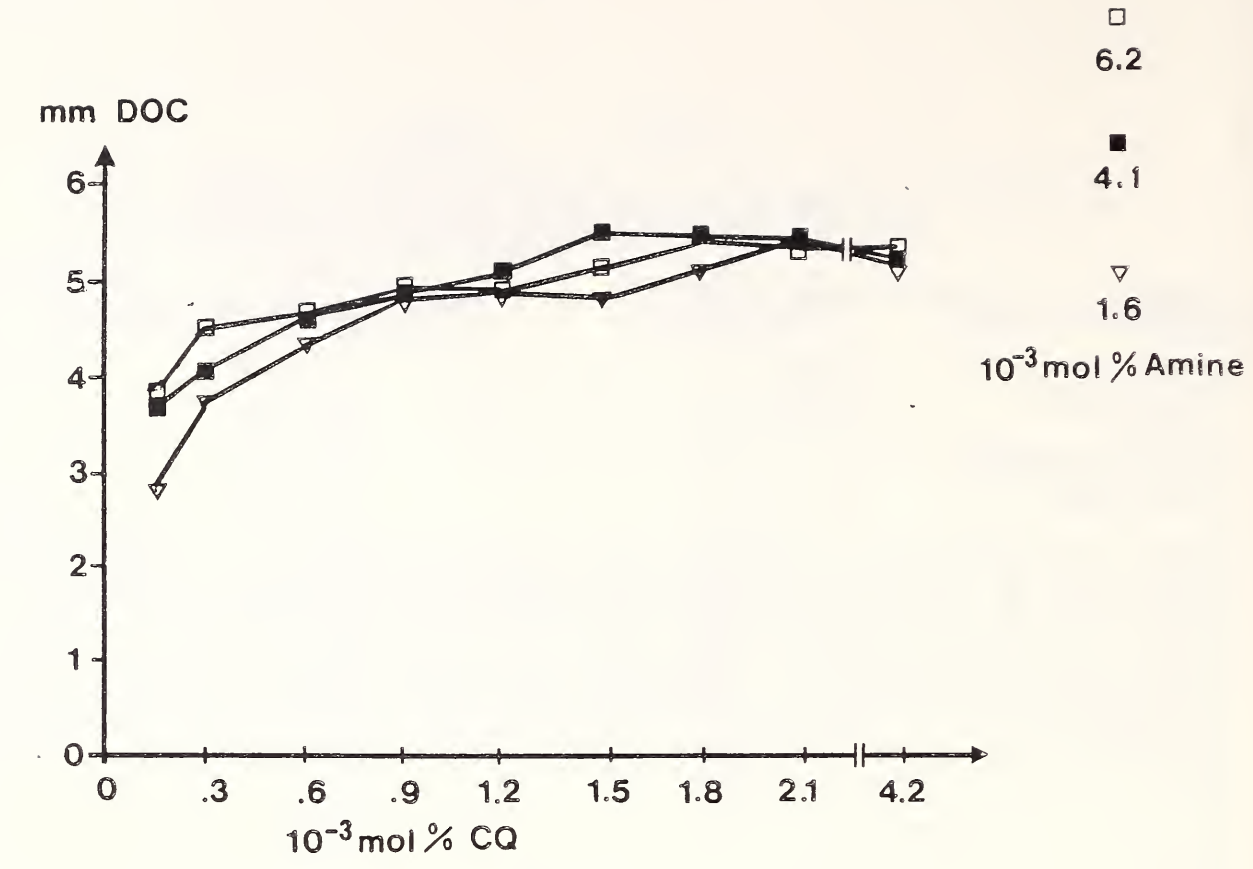


Figure 3

Depth of Cure (DOC) at Constant Amine (4-EDMAB) Concentrations as a Function of CQ Concentration.

6×10^{-3} mol % Amine

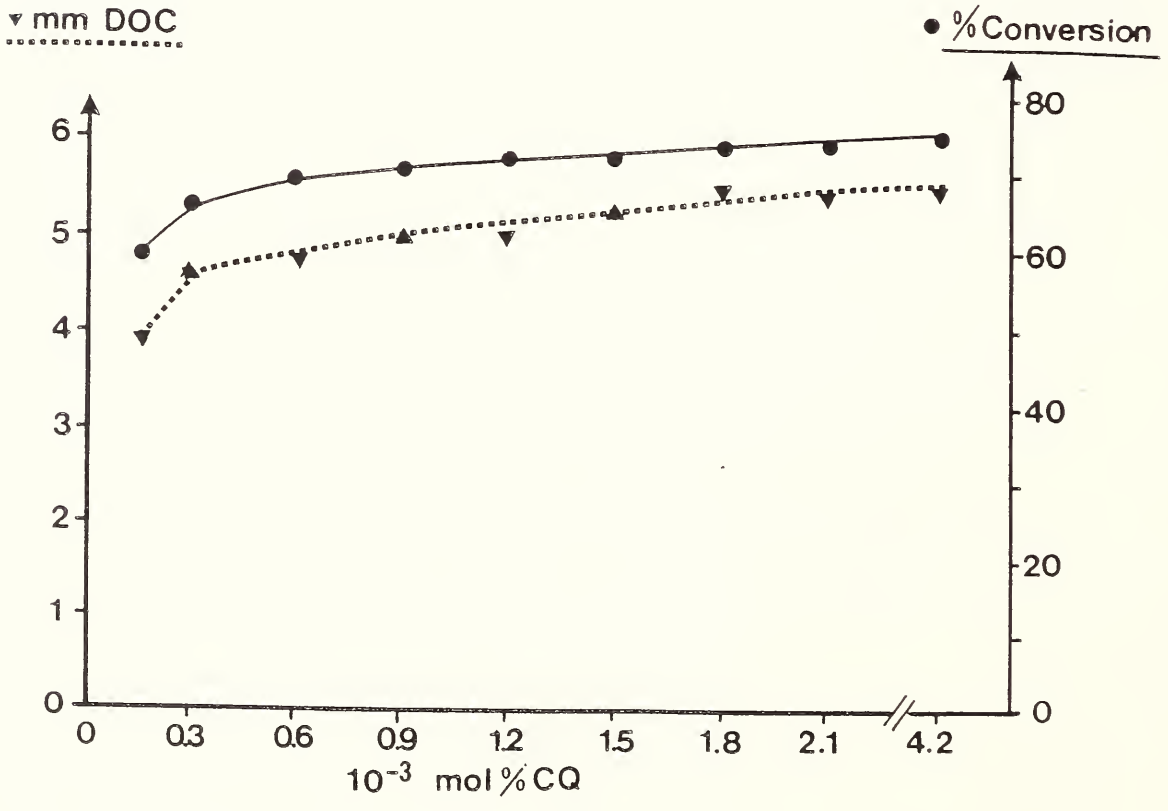


Figure 4

DOC and Conversion as a Function of CQ Concentration at Constant 4-EDMAB Concentration.

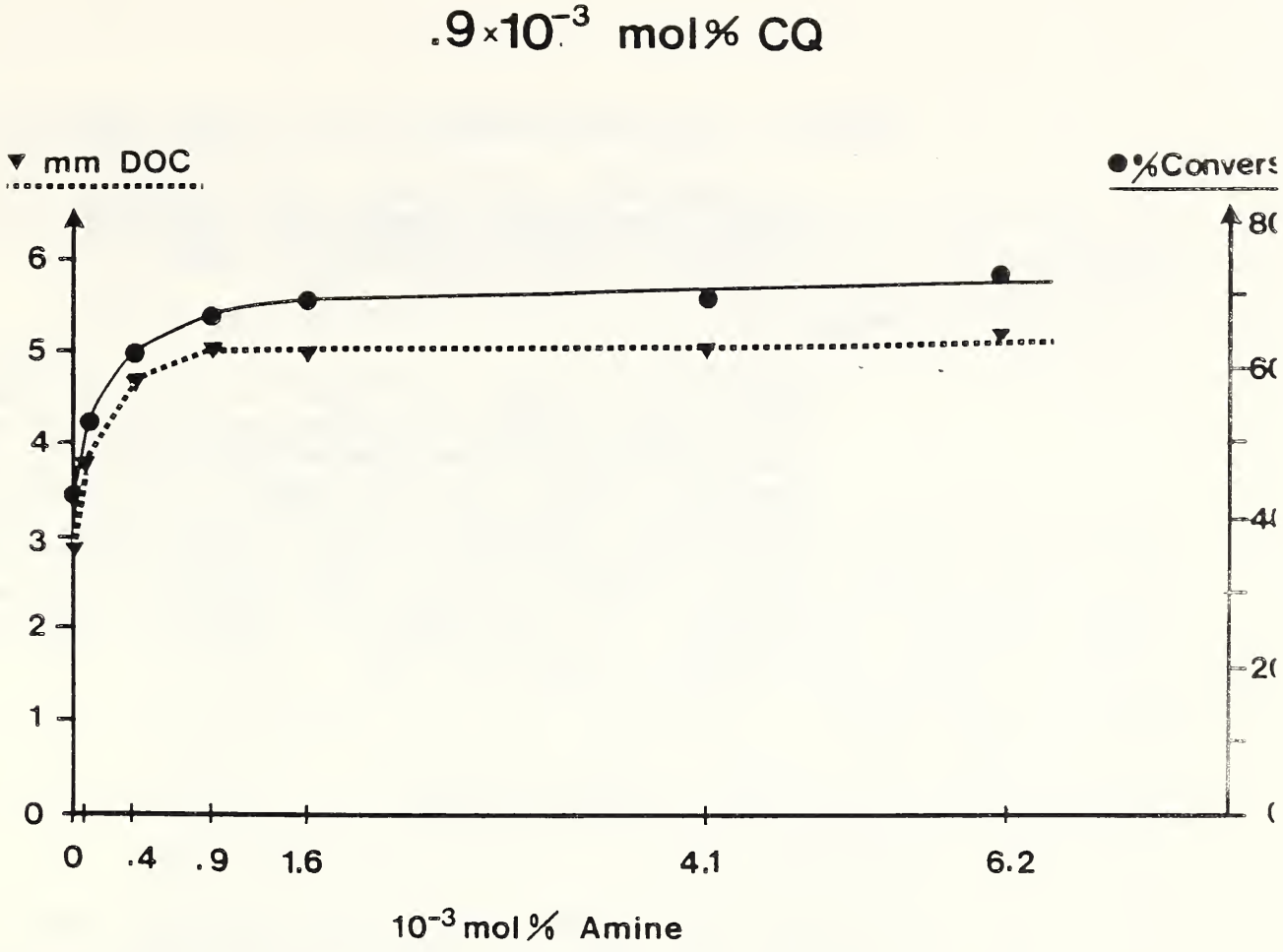


Figure 5
DOC and Conversion as a Function of 4-EDMAB Concentration at Constant CQ Concentration

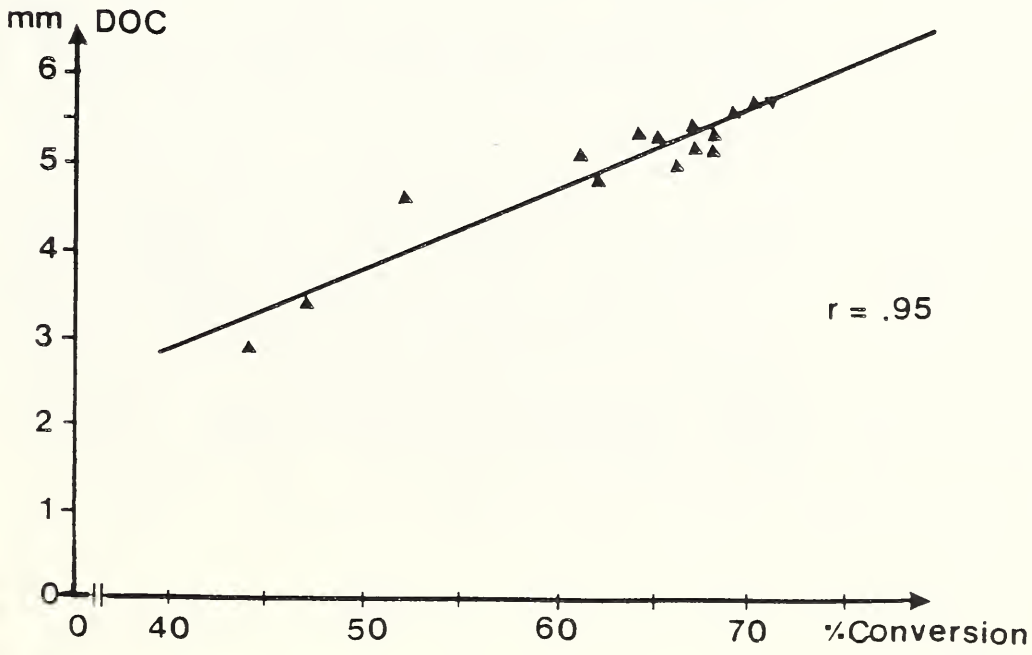


Figure 6
Correlation of DOC and Conversion

Phase II. Prototype Composite for Clinical Evaluation

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

Phase III.

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

II. Improvement of Dental Cements

Overview

Although used in relatively small quantities, dental cements are essential in a number of dental applications as: (a) temporary, intermediate and, in some cases, more permanent restoratives, (b) cavity liners and bases, (c) luting agents to bond preformed restorations and orthodontic devices, (d) pulp capping agents and endodontic sealers, and (e) impression pastes. This wide range of dental uses makes it virtually impossible for one type of cement to have all the necessary properties demanded in these diverse applications. Therefore, there is a need to develop "tailored" dental cements with 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 and flexural strengths.

Phase I. Formulation and Evaluation of New Cements

(a) Resin-Modified Glass Ionomer Cements

The feasibility of developing hybrid dental cement-composites (HCC's) from polyelectrolyte based cements, e.g. glass ionomer cements, using compatible vinyl monomer and initiator systems was demonstrated. These resin modified cements exhibited a significant improvement in diametral tensile strength, but somewhat lower compressive strength, microhardness and wear resistance. Unlike glass ionomer cements or their metallized versions (the cermets), HCC's displayed a markedly reduced incidence to catastrophic failure and improved chemical resistance to degradation resulting from exposure to acidic environments. During the dual setting process, HCC's are less sensitive to excessive hydration and, after curing, less prone to dehydration than glass ionomer cements. When used as the base material for indirectly bonding resin-based composites to dentin via the glass ionomer cement composite sandwich technique [45], HCC's do not require prior etching and/or the use of intermediary bonding agents to achieve a satisfactory seal against microleakage. By varying the monomer system and/or the initiator systems, it is possible to formulate a number of different types of HCC's including a visible light activated formulation (Tables 12). A patent has been applied for relating to this new class of hybrid cement-composites.

(b) Formation of Hydroxyapatite in Hydrogels from Tetracalcium Phosphate/Dicalcium Phosphate Mixtures (New)

In collaboration with Drs. L. Chow and S. Tagaki of the American Dental Association Health Foundation, Paffenbarger Research Center (APAHFPRC) and Dr. A. Sugawara, of Nihon University, we are investigating the feasibility of developing hybrid cement-composites based on the formation of hydroxyapatite and other calcium phosphates in hydrophilic, crosslinked matrices (hydrogels).

Apatitic calcium phosphate cements, formed by the ambient reaction of tetracalcium phosphate (TTCP) with dicalcium phosphates (DCP), were recently reported [46]. H_2O or dilute aq. H_3PO_4 (0.2%) is used as the liquid vehicle for this reaction. In this preliminary study, we hope to ascertain if

TABLE 12

FORMULATION OF HCC COMPOSITES

COMPONENT	FUNCTION
BLENDED POWDER (POLYACID + ION-LEACHABLE GLASS, CERAMIC)	PROVIDES COMPONENTS FOR IONIC HYDROGEL COMPOSITE FORMED BY ADDITION OF H_2O
2-HYDROXYETHYL METHACRYLATE (HEMA) HYDROXYPROPYL METHACRYLATE (HPMA)	WATER COMPATIBLE VINYL MONOMERS FOR FORMATION OF NONIONIC MATRIX
POLYETHYLENE OXIDE DIMETHACRYLATES (PEGDMA), GLYCEROL DIMETHACRYLATE (GDMA) 4-EGDMA, BIS-GMA, UDMA, ETC.	CROSSLINKING VINYL MONOMERS THAT CAN BE USED WITH HEMA/H_2O
HYDROGEN PEROXIDE (HOOH) 30% b.w. AQUEOUS SOLUTION	HEMA/WATER COMPATIBLE FREE RADICAL INITIATOR
ASCORBIC ACID, Ca ASCORBATE, ETC. (AA)	ACTIVATOR FOR AMBIENT DECOMPOSITION OF HOOH AND OTHER PEROXIDES
CUPRIC SULFATE (PENTAHYDRATE) ($CuSO_4 \cdot 5H_2O$) IRON SALTS (e.g. $FeSO_4$, $Fe_2(SO_4)_2$ etc.)	CO-ACTIVATOR FOR HOOH/AA INITIATOR SYSTEM
CAMPHORQUINONE (CQ)-VISIBLE LIGHT BENZOIN - UV	PHOTOCHEMICAL INITIATOR
ETHYL 4-DIMETHYLAMINOBENZOATE (4EDMAB)	PHOTOACCELERATOR
SODIUM p-TOLUENESULFINATE ($CH_3PhSO_2Na \cdot 2H_2O$)	LATENT INITIATOR/ACTIVATOR
3-METHACRYLOXYPROPYL-TRIMETHOXYSILANE (A-174)	SILANE COUPLING AGENT FOR INTERFACIAL BOND FORMATION WITH SiO_2, Al_2O_3 AND SIMILAR PHASES IN FILLER
SURFACTANT VINYL MONOMERS (E.G. PMDM, PHOSPHORYLATED AND PHOSPHONATED BONDING AGENTS)	FOR BONDING TO OTHER PHASES IN COMPOSITE.

hydroxyapatite (HAp) can form in self-cured hydrogel composites containing TTCP/DCP mixes. The setting times (ST) and diametral tensile strengths (DTS) of several hydrogel composites were determined. The hydrogels were of two types: (1) vinyl thermosets derived from the copolymerization of HEMA (2-hydroxyethyl methacrylate) and crosslinking monomers, and (2) polyelectrolyte based hydrogels formed from aq. poly(alkenoic acids), e.g. poly(acrylic acid). Cylindrical specimens 6 mm D X 3 mm H were prepared and stored in H_2O for up to 30 days. The HEMA composites were hardened in 7-15 min by free radical initiation (benzoyl peroxide/tertiary aromatic amine). The polyelectrolyte cements harden in 6-8 min. After various periods of H_2O storage at 37°C, some of the specimens were examined by X-ray spectroscopy for HAp. HAp formation was not found in the HEMA composites even after 30 days of H_2O storage but was detected in the polyacid cements after 24h. 24 h DTS values of the HEMA composites (22-26 MPa) were higher than those of the polyacid cements (7-12 MPa). However, the latter are comparable to commercial zinc polycarboxylate cements. Both the H_2O content and initial pH may be factors controlling the rate and extent of HAp formation in hydrogel composites containing TTCP/DCP mixtures.

An abstract has been submitted for the 1988 IADR meeting based on this work.

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

Overview (Filler)

On a weight basis, the major component of dental composites is usually the reinforcing filler (e.g., 50-86%). For many properties of the composite, the volume percent of the dispersed phase is a more significant parameter. The reinforcing filler performs many functions in a composite such as stiffening the lower modulus resin binder, thereby increasing mechanical properties, enhancing dimensional stability, moderating the exotherm of polymerization and the mismatch 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 [47-51].

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 [47,48]. Properly done, this results in a glass filler having superficial surface porosity into which the resin can flow and mechanically interlock on polymerization, thus complementing the usual bonding through silane coupling agents.

The search for dental composites of superior wear resistance for use in stress-bearing applications has spurred research into new types of stable fillers of sizes and shapes conductive to optimal packing efficiency. New techniques to significantly increase filler loadings have appeared in [49,50].

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 [52]. 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 [51,53].

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 [52]. 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 [51-53].

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

Objective

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

PROGRESS REPORT

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

The objective of this part of the overall study on developing effective interfacial bonding between the resin and filler phases of composites and cements was to determine the feasibility of applying silane coupling agents to nonsiliceous fillers. A conventional silane coupling agent, 3-methacryloxypropytrimethoxysilane (MAPS), and an experimental multifunctional silane agent derived from BIS-GMA and 3-isocyanatopropyltriethoxysilane, designated BIS-GMA/IPTES [53,54], were applied to β-tricalcium phosphate powder and to both a crystalline form (β) and a vitreous form of calcium metaphosphate. Preliminary results indicate that high temperature (100-170°C) treatments are needed to bond these silanes to these fillers (determined by IR spectroscopy and the hydrophobic behavior of a drop of water on the powders after thorough washing of powders with solvents). While the mixing and dispersion of these fillers in dental resins is improved by these treatments, the diametral tensile strengths of their composites is not increased over that of similar composites prepared with untreated fillers. Our previous studies with a conventional radiopaque glass filler clearly demonstrated the superiority of composites prepared with silanized fillers [53].

Phase II. To Develop Improved, More Durable Interfacial Bonding Systems and Fillers for Composites and Cements. (Filler Portion of Project is New.)

Filler Systems Based on Calcium Metaphosphates

This project represents a collaborative effort with B. Fowler of NIDR. Orthophosphate minerals such as tricalcium phosphate and apatites have been studied as fillers for dental composites [55,56]. Due to the large mismatch in their respective refractive indices, composites based on apatitic fillers and the usual dental resins are esthetically deficient and unsuited for photopolymerization. Calcium metaphosphates (CMP's) are a unique class of phosphate minerals $[Ca(PO_3)_2]_x$, possessing polymeric structures analogous to that of silicates and refractive indices optically compatible with resins such as BIS-GMA. The aim of this study was to prepare several types of CMP's and evaluate their potential as fillers for visible light activated (VLA) dental composites. The vitreous and β-crystalline forms of CMP were prepared by controlled thermal dehydration of calcium dihydrogen phosphate hydrate:

$$Ca(H_2PO_4)_2 \cdot H_2O \xrightarrow{\Delta} Ca(PO_3)_2 + 3H_2O\uparrow$$

Hybrid fillers based on silica and CMP's also were prepared by thermal methods. CMP fillers were characterized by IR spectroscopy and optical microscopy. Conventional grinding techniques (e.g. ball milling) were used to prepare fibrous particles in several size ranges, e.g. 1-25μm. Composites were formulated using VLA BIS-GMA and similar resin systems. Both untreated and surface modified (e.g. silanized) CMP's were used (typical filler loadings = 40-80 wt%). Depths of cure were 5-7mm after 40s irradiation with a blue light. Vitreous CMP and its siliceous hybrid versions were soluble and reactive in water and yield composites which expanded but were of low strength, (24 hour DTS = 8 MPa). Composites based on the insoluble β-CMP were more moisture-resistant and had higher DTS values (12-28 MPa). [At these stress levels, a tendency to arrest brittle fracture was noted.] Conventional silanizations improved the dispersability of these fillers in composites but not their DTS's. Through the proper selection of filler systems, it may be possible to compensate for polymerization shrinkage. A number of other types of coupling agents and surface modification procedures are under consideration for use with these novel fillers.

An abstract based on this work has been submitted for the 1988 IADR meeting.

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

Objective

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

Overview

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].

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, three types of adhesion-promoting systems have demonstrated rather strong adhesion to dentin. One system involves pretreatment of dentin with an aqueous solution of 2-hydroxyethyl methacrylate (HEMA) and glutaraldehyde [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 comonomer such as NPG-GMA or NTG-GMA and PMDM, the diadduct of HEMA and pyromellitic anhydride [8,15,16]. The latter two bonding systems display significant adhesion to enamel as well as dentin.

PROGRESS REPORT

Phase I. Synthesis of Carboxylic Acid-Containing Monomers

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

A surface-active monomer analogous to PMDM, was prepared from 3,3',4,4'-benzophenonetetracarboxylic diahydride (BTDA) and t-butylaminoethyl methacrylate (TBAEM). The reaction was carried out in methylene chloride by adding dropwise a solution of TBAEM in this solvent to a stirred solution of BTDA at room temperature. Two moles of TBAEM were used to one of BTDA to yield the diadduct as a viscous yellow liquid after removal of the solvent. Purification by trituration

with cyclohexane yields a purer product which slowly solidifies on standing. This monomer is polymerizable by exposure to UV irradiation. IR analysis supports the structure of this coupling agent as having difunctional amidoethyl methacrylate and free CO_2H groups. The benzophenone unit in the structure confers photoactivity on this monomer.

A similar synthesis involving TBAEM and PMDA has been completed and purification and analysis of the product is in progress.

Phase II. Synthesis of Dentinal Bonding Agents

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

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

Antonucci, J.M. Discussion Leader for Gordon Conference on Adhesion, New Hampton, NH (Aug. 1986).

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

This task is divided into the following sections:

A. Wear and Durability Assessments of Composite Restoratives

Phase I. Recent Commercial Composites Which Appear Promising for Posterior Occlusal Application.

Phase II. Experimental Composites with Flexible Polymers.

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

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

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

Phase VI. Assessment of Wear of Human Enamel Against Conventional Porcelain and New Castable-Ceramic Counterfaces (new task).

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

C. Wear Instrumentation

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 on *in vivo* worn restoration biopsies revealed that both mechanical wear and the intraoral environment play an important role in the degradation of composite restorations. For this reason, we believe that a relevant 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 have found that increasing the degree of cure decreased the extent of softening and improved the wear resistance of the specimens which would otherwise be damaged from preconditioning [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 margin 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.

The solubility parameter for the resin approximated that of pure ethanol(2.6×10^4 $J^{1/2}$ $m^{-3/2}$). Accordingly, with the microhardness and wear tests, ethanol and water were used as preconditioning fluids (for the latter no effect is expected).

From changes in hardness, it was apparent that considerable matrix softening resulted from the penetration of ethanol. On the other hand, the wear was essentially unaffected. This result is attributed to the high degree of crosslinking which, in this case, permits some diffusion, but very limited dissolution from organic solvents.

Although the wear of the PFUMA/BIS-MPTMS system appeared to be unaffected by ethanol preconditioning, the absolute hardness was less and the wear much larger [5] than that observed for the more conventional resin-based composites. For this reason we have initiated a study involving composites with resins of a higher fluorine content and greater flexibility. The descriptions and performances of these composites are presented in the Progress Report section which follows.

The inorganic reinforcing filler was evaluated by preconditioning commercial dental composite specimens in weak intraoral acids which may damage the filler and the interface. Composites employing modified glasses with alkaline-earth elements to obtain radiopacity were more sensitive than the pure silica- reinforced composites. It was determined that corrosion plays an important role in the degradation of composite restorations as evident from the leaching experiments of Söderholm [6,7] and the wear and hardness measurements made at NBS [8]. The reason for including Phase V (appatite 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 [9].

Since glass-ionomer cements show some bonding properties to dental tissue [10], 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 [11]. Specimens preconditioned in dilute lactic acid revealed considerable chemical dissolution as apparent from electron micrographs and accelerated wear. More recent work [12] 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 modifications in the composition and structure of this class of materials for enhanced durability.

The so-called hybrid cement-composites (HCC) formulated at NBS 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 (See Part I, Section F). 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].

A manuscript describing our work (previous reporting period) on the silver-sintered glass-ionomer cement has been submitted to the Journal of Dental Research.

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.

The experiments involved 10 treatments for each specimen. Each treatment comprised a six-minute immersion in the topical fluoride

agent and water as a control. The mass of each specimen was determined by weighing to within 10 μg before and after each treatment. The wear was measured after the final treatment and compared with that for the control. More details and results are contained in the Progress Report section which follows.

One concern in the application of posterior occlusal restorations is the amount of wear on the opposing enamel surface caused by abrasion with the restoration. Using the pin and disc (specimen) wear apparatus we have used the wear of the pin as a measure of the severity of this problem. We have found that the conventional composites (although not recommended for posterior application) produce the most wear on the stainless-steel pins, and the microfills, the least. In collaboration with the Naval Dental School, we are addressing this problem more systematically with respect to porcelains and castable ceramics. The details and preliminary results are discussed in the Progress Report section.

PROGRESS REPORT

Phase I. Recent Commercial Composites Which Appear Promising for Posterior Occlusal Application.

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 NBS experimental composites. At a later time we will very likely conduct some evaluations of other selected commercial posterior composites.

Phase II. Experimental Composites with Flexible Polymers

Studies on visible-light activated composites comprising flexible resins with low solubility parameters and low polymerization shrinkage have continued through this reporting period.

Although PFUMA/BIS-MPTS based composites appeared to be little affected by the preconditioning procedure, the hardness and wear resistance were considerably lower than that observed for more conventional resin-based composites [5]. For this reason we initiated a study on a composite with a resin of higher fluorine content to achieve more flexibility, thus a higher degree of cure. The resin contains a 70/30 mixture of polyfluoromethacrylate and hydrocarbon diluent monomers along with a photoinitiater, a camphorquinone/tertiary amine, for visible-light activation. The polymerization shrinkage was reduced by employing a prepolymer of PFMA with 10 repeat units corresponding to a molecular weight of 10,320 g/mol. The experimental composite contained 69 wt.% fine (2-4 μm) silanized fused quartz. Both the environmental resistance, as determined by Knoop Hardness

Number (KHN), and wear resistance were considerably improved over that for the PFUMA/BIS-MPTS composite. In addition, the environmental resistance of the PFMA composite was much better than that for more conventional dental composites containing rigid resins, e.g., BIS-GMA. The steady-state wear approximated that observed for a microfilled composite. The results of this study were presented before the IADR conference in March 1987 [13].

The potential for improving the properties of the PFMA system was realized by employing a dual-cured (photochemical/chemical) system. The system currently under investigation is similar to the PFMA system mentioned above, except the current one is a powder-liquid system with silanized fine fused quartz containing benzoyl peroxide for chemical activation. (See Section I-F). Two advantages are achieved from the dual-cured system: (1) the degree of cure is higher than that for the corresponding visible-light activated or chemical system, and (2) we found that the depth of cure gradient obtained from solely visible-light activation is essentially eliminated (See Section I-F). The preliminary results revealed that the KHN of the dual-cured neat resin was about four times as large as that for either the corresponding visible-light activated or chemically cured resin. The KHN of the dual-cured composite, 55 kgf/mm^2, was larger than that observed for any of our experimental flexible resin-based composites. The KHN fell only 27% after storing in ethanol for one week which compares favorably with 70% for a BIS-GMA based composite we have tested [2]. The wear resistance for the water-stored specimens fell between that characteristic of a conventional composite and a microfill, but marginally increased for the ethanol-stored specimens, which may be an indication of mild corrosion of the filler by water.

An abstract summarizing this work has been submitted to the IADR for the conference in March 1988.

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

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 [14] with the silver nitrate staining technique [15] 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 work on the effect of topical fluoride treatments on commercial dental composites has been continued during this reporting period in collaboration with the University of Maryland Dental School. The procedure (as described in the Background section) on a commercial, radiopaque, visible-light-activated composite involved treatments in distilled water (control), 0.5% acidulated phosphate fluoride (APF), 1.23% APF, 0.4% SnF_2, and 1.1% NaF. According to preliminary results, only the APF gels produced significant leaching for which a maximum loss of 150 μg (0.01%) was observed over the ten treatments using the 1.23% APF gel. The wear appeared to be accelerated in the early region (where more damage is likely) using this gel; however, the variability is too high to make reliable determinations at this time.

Similar measurements have been initiated on a commercial microfilled composite employing a silica filler.

An abstract summarizing this activity has been submitted for the IADR Conference in March 1988.

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

This phase has not been initiated as yet. As stated earlier radiopaque composite fillers employing alkaline earth-modified glasses are sensitive to corrosion from the intra-oral 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 NBS. If these appear to be promising, some wear and environmental resistance studies on corresponding composites may be done during the next reporting period.

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

In collaboration with the Naval Dental School wear measurements on human tooth enamel against rotating counterfaces of a conventional porcelain and a new castable ceramic (Dicor) have been initiated. The preliminary results showed that the wear resistance of enamel with respect to the unglazed ceramic was better than that with respect to the porcelain. However, if the ceramic is glazed as per manufacturer's instructions, then the wear resistance of the enamel with respect to the porcelain is superior.

An abstract summarizing the results of this work has been submitted for the IADR Meeting in March 1988.

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

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 [16]. 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 former, 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.

The values of T_g as a function of cure temperature have been determined using a Weisenberg rheogoniometer. This instrument employs a forced vibration (mechanical) method and measures a complex modulus in shear comprising a component of stress in phase (elastic modulus), and one 90° out of phase with the strain with sinusoidal time dependence. The 90° component, called the loss modulus, goes through a maximum with temperature. The temperature corresponding to the maximum loss tangent (loss modulus/elastic modulus) may be arbitrarily defined as T_g which, of course, depends upon the frequency.

The values of the in phase component, called the storage or elastic modulus, and its temperature dependence are also important in regard to assessing the performance of these materials. These values describe the rigidity of the material from which the temperature at which the restoratives break down under stress may be determined.

Using the Weisenberg rheogoniometer, the cure temperature dependence of T_g has been determined [17] 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_∞}.

PROGRESS REPORT

No activity was undertaken on the measurement of T_g during this reporting period. The rheogoniometer has been disassembled and returned to its owner and, accordingly, is no longer available for our use. We are exploring the possibility of using a less complicated device to obtain this information. For example, using an ultrasonic device, both T_g (although at a much higher temperature) and the elastic modulus may be obtained from the phase velocity and attenuation.

A manuscript describing the results on the BIS-GMA and the BIS-GMA/TEGDMA systems has been submitted to the Journal of Dental Research.

C. Wear Instrumentation (New Task)

Background

The wear measurements mentioned throughout this chapter were made using a pin on disc apparatus described in Reference [18]. The original version was designed and assembled at the University of Indiana [19]. 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 [18]. This modification resulted in a more convenient, flexible, and reliable system, which has been used up to the present time. The next version is now being assembled, for which the salient features are described below.

Phase I. Methodology for Improved Wear Apparatus

As a consequence of increased demand and modified methodology in dental wear measurements, a new pin on disc wear apparatus is being designed and assembled. The new version calls for 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.

If funding permits, additional instrumentation will be provided to measure friction during the course of wear. Torque monitoring devices are now commercially available. An important feature to be incorporated is the facility to conduct submerged wear tests in selected media. (In the present version, fresh distilled water at 37°C flows over the specimen surface continuously.) An effort is being made to use generic commercial components and modular devices as much as possible to facilitate repair and replacement of defective components.

The computer, which will control the apparatus, has the capability to do calculations for data processing including statistics, and thus will not require 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.

A large portion of the electronic components for the new wear apparatus have been acquired, assembled, and tested during this reporting period. These include the computer (programmable in BASIC), hard and soft disc drives, data acquisition control unit, integrating voltmeter, 20 channel relay multiplexer with thermocouple compensation, a 16 channel general purpose switch, and a printer. The stepping motors, their power supply and control circuits, encoders, and LVDT's and their conditioning circuits will be acquired and assembled during the next reporting period.

Phase III. Completion of the Apparatus, Including Design and Assembly of the Mainframe.

After the three drive units and related equipment have been obtained, it will be possible to design the mainframe for the mechanical portion of the apparatus around these components. This task is expected to be completed during the next reporting period.

D. Clinical Examinations Employing Removable Partial Dentures

Background

In order to evaluate the clinical significance of the effects of post curing of composite resins, a clinical study was initiated in cooperation with the ADA, using partial dentures teeth as a means of placing composite resins retrievably in the oral environment.

The design of this study has been previously reported [1].

Accomplishments

Phase I. The retrieval of all denture teeth with composite resin restorations and replacement of these teeth with new denture teeth and establishing proper masticatory and esthetic function of the prostheses.

The entire clinical aspect of this study has been completed.

Phase II. Photographic Records and Clinical Evaluation.

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

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

Both aspects of Phase II have been completed and results were reported at the IADR, The Hague, The Netherlands June 26-28, 1986.

Phase III.

No phase III incorporated in proposal; inadvertently skipped in the numbering.

Phase IV. Measurement of Lost Volume of the Worn Restorative Resins

(a) Evaluation of the technology developed by the NBS Metallurgy Division for measuring the galling of metals.

Some preliminary results were obtained on composite resins with the profilometer of the Metallurgy Division. Sample positioning proved to be a problem because of non standard specimen size (denture teeth). Successful plots of the resin surface were obtained and a quantitative measure was obtained of the lost volume of the composite. The evaluation showed that quantitative information can be obtained with a profilometer.

(b) A profilometer was designed similar to the one in the Metallurgy Division, but with significant modifications. Part of the modifications were made on the advice of Dr. Swanson at the Technical Center of the John Deere Company who has a profilometer also patterned after the original Materials Science Division Unit.

The profilometer was designed and is currently being assembled with independent X and Y positioners under computer control with a fixed LVDT for measurements in the Z direction.

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III. DENTAL ALLOYS, CERAMICS AND METROLOGY

Overview

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

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

PROGRESS REPORT

Overview

Residual stress from the porcelain firing cycle is considered to be a major factor leading to failure of porcelain fused-to-metal restorations. This study 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.

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. 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), determination of the Weibull fracture stress distribution and integration of the two into reliability analysis.

Phase I. Complete Development of the Required Finite Element Model (FEM)

This model has been developed and has been used to first study the effects of build-up of residual stress in a slab of porcelain cooled from the firing temperature. It includes effects of cooling rate, temperature distribution, cooling rate dependence of the glass transition temperature (T_g) temperature dependent thermal expansion below T_g, coefficient of expansion above T_g, and temperature dependent modulus. This phase is completed.

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

Results show that the stress profiles are as expected for a tempered glass. This lends confidence in the FEM and encourages continuance of this approach. The results show that the following equation aptly describes the surface stress, σ, as a function of the cooling rate, q, and the half thickness of the porcelain slab, ℓ,

$$\sigma = k\ell(q/q_o)^n$$

Here, q_o is a reference cooling rate. For Ceramco® porcelain, k = 1.016 MPa-mm^{-2}, n = 1.03, for (Vita Zahafabriek) porcelain, k = 0.856 MPa-mm^{-2} and n = 1.04 Vita.

A very important result is that the surface residual stress can be strongly affected by the coefficient of thermal expansion of the glass (porcelain) <u>above</u> the T_g. This alone apparently invalidates any attempts at describing compatibility of porcelain-metal systems by use of purely elastic consideration below T_g as the porcelain-metal system is only a modification of an all porcelain one.

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

This phase is in progress.

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

This phase will follow Phases I-III.

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

Phase VI. Extend Results (of FEM and Those from Part B (Following) of Porcelain-Alloy Compatibility) to Reliability Analysis.

This is a new phase. The real possibility exists that reliability will be more meaningful than compatibility.

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.

The effect of reglazing a dental porcelain after fracture on the strength of the porcelain has been evaluated. Ten (10) PFM samples (3 x 11 x 60 mm alloy strips with 11 x 11 x 1.5 mm porcelain tablets embedded in the surface) were made from a commercially available alloy and porcelain. Multiple fractures were obtained (on the same specimen) in a universal tester (cross head speed 0.1 mm/min). The samples were then reglazed. The first reglazing involved heating the samples at 65°C/min to 990°C (1825°F) and air quenching. The samples were then fractured again and subsequently reglazed. This time the reglazing procedure was to heat to 882°C (1625°F) and hold for 3 minutes, then continue to 982°C (1800°F). The fracture data could be fit to a Weibull distribution, as previously reported (AADR 1986 #752). The values for the characteristic strength S_o and the Weibull modulus m are given below.

Procedure	#Fractures	m (CI*)	S_o (MPa)	(CI*)
Glaze	16	3.8 (3.2-5.4)	21.8	(20.7-25.0)
Reglaze	20	3.2 (2.6-4.5)	14.4	(12.7-16.7)
Reglaze & Hold	19	2.6 (2.1-3.7)	21.0	(17.2-24.6)

*CI notes the confidence interval calculated with the tables of Thoman, Bain and Antle.

The above values were obtained from the least square fit on a Weibull probability plot. The confidence limits show that the down-ward trend in the Weibull modulus is within the statistical fluctuation. Reglazing does not appear to have a major negative effect on the PFM system strength.

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

The specimens have been prepared for the evaluation of the change in system strength due to the addition (50% by volume) of powdered alumina (25 μm particle size) to a commercial porcelain frit. The coefficient of thermal expansion was reduced from 10.8 to 7.5 x $10^{-6}\,°C^{-1}$ to (40-400°C). Fracture data have been obtained but results are not available at this time.

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

This phase will follow 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 effect 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.

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 [1].

A primary effort at NBS has been the development of a method for evaluating the ability to cast an alloy to fill a mold under prescribed casting conditions. For this purpose a method employed a polyester-grid mesh pattern has been chosen. (see NBSIR 87-3539, 1987 for more details)

Accomplishments

Phase I. Evaluation of Mold and Alloy Temperature Effects

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

Phase II. Analysis of Effects of Composition on Castability

A manuscript entitled "Mesh Monitor Casting of Ni-Cr alloys; Element Effects" has cleared internal review (WERB) and will be submitted to the J. of Dental Materials for publication.

Phase III. Analysis of Effects of Investments on Castability.

A rudimentary study was made on the effects of batch variations of investments and "brand" variations on the transformed castability value

$$C_{v,t} = a + b\ T_A^{1/2} T_M^2$$

where T_A is the alloy superheat temperature, $T_A = T_C - T_S$,

T_C = alloy casting temperature

T_S = alloy solidus temperature

T_M = mold temperature.

The results indicate:

1) Investment batch changes affect the intercept "a" but the temperature coefficient "b" is unchanged (for a given alloy),

2) An alloy may show changes in both "a" and "b" when using a second investment,

3) In some instances, an alloy may behave virtually the same in two different investments.

The results indicate how much of an effect a change in only investment batch can have on processing in a dental laboratory. For one case, a difference in "a" of 0.37 was observed between two batches. This can result in a 20% difference in castability values, i.e. processing would be significantly affected.

D. Castability (Accuracy of Fit of Dental Castings)

PROGRESS REPORT

Overview

Previous measurements have indicated that the setting expansion at the site of the wax pattern in a phosphate bonded casting investment is significantly less than the expansion observed in the external dimensions of the investment [2,3].

It could be argued that the reduction in observed setting expansion is due to inadequate coupling of the investment to the strain gauge. Experiments by Marsaw et al also showed a reduction in setting expansion, as determined by a method not involving strain gauges. To provide a definitive assessment of the coupling between the strain gauge and the casting investment, a study was initiated to determine the thermal expansion of a phosphate bonded investment by means of a strain gauge.

Accomplishments

High temperature strain gauges have been identified and obtained with an active temperature range of 0° to 850°C. Methacrylate mounting frames have been developed to provide structural rigidity during the investment process. The absence of a polyamide backing on the strain gauges prohibits the use of the technique developed by Engler et al.[4].

The mechanical strength and durability of the gauge have been found to be minimal. A special electrical insulator of a refractory material has been designed to provide both mechanical support and electrical insulation of the lead wires to the system.

E. Solderability

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

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

No effort during FY87. Work was concentrated on other topics in this section.

G. Metrology and Analysis: Occlusal Force Indicator

This effort was delayed in order to concentrate on Weibull statistics and related analyses.

H. Metrology and Clinical Performance

Overview

This part of the program involves the application of the disciplines of fracture mechanics and the statistical theory of fracture to the study of dental materials.

Accomplishments

Phase I. Development of Data Reduction Software

A software package specific for our needs has been developed that greatly facilitates the use of the Weibull distribution.

In particular the transformation of the cumulative probability distribution function F(s) as a function of applied stress, as defined by Weibull, yields

$$F(s) = 1 - \exp\,(-S/S_o)^m$$

$$\text{then} \qquad \frac{1}{1-F} = \exp\,(S/S_o)^m$$

$$\text{and} \quad \log \log \left(\frac{1}{1-F}\right) = m\text{Log } S - m\text{Log } S_o$$

Thus a log log (1/1-F) plot vs log S should yield a straight line with slope m.

The linearity of this plot is a measure of how well a Weibull distribution is applicable to the data under discussion. This assessment of the data was performed in the past with Weibull probability paper, a far more cumbersome method.

The software for performing the plotting; as well as a least square fit on the plot to determine the slope m and the intercept mLong S_o is complete, and has been used to determine the values for 4 different dental porcelain-fused-to-metal systems data, as determined by 4 point bending.

These results (shown in Table 2 and Fig. 1A-1D) have been accepted for inclusion in Biomedical Engineering VI.

Phase II. Analysis of Resin-Metal Bond Tests

A series of data on a composite resin to metal bond tests as performed by Dr. Van P. Thompson at the University of Maryland has been evaluated. It was found that for several of the bond systems a special form of the Weibull distribution applies, i.e. the exponential distribution with the Weibull parameter $m \simeq 1$. Many of the systems had a value of $1 < m < 2$ producing a very asymmetric cumulative failure distribution which describes the data adequately; however this is a description of the data which is not possible with a Gaussian distribution of the data. Part of these results have been presented by Drs. Thompson and de Rijk at the Engineering Foundation Conference on the Application of engineering to dental prostheses.

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

For the DTS (diametral tensile strength) data obtained for a commercial composite resin the LogLog (1/1-F)) vs Log S curve showed a marked non linearity. It has been proposed by Saunders and in a slightly different form by K.K. Phani, that a mixed distribution may best describe the data.

The equation for the bimodal distribution is

$$F(s) = 1 - \alpha \exp -(S/S_1)^{m_1} - (1-\alpha) \exp (S/S_2)^{m_2}$$

with m_1, m_2 the Weibull moduli

S_1, S_2 the scale parameters or characteristic strengths

and α = Weighting factor

When this is applied to the data obtained for the composite resin submerged in either heptane, Ethanol (70%) or distilled water the results presented in table II are obtained.

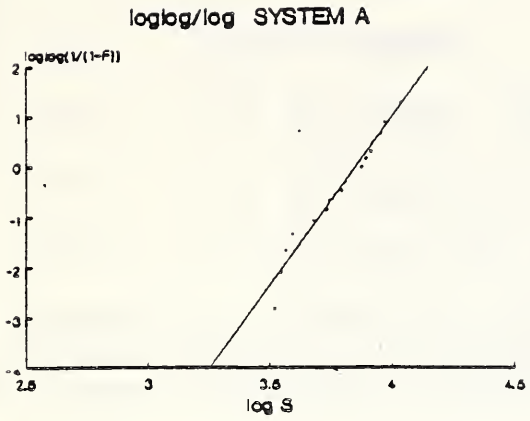

Fig. 1A

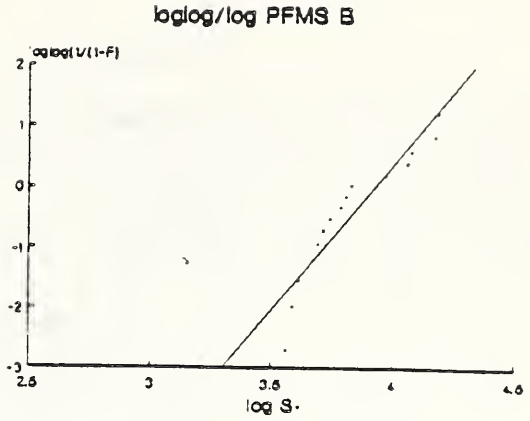

Fig. 1 B

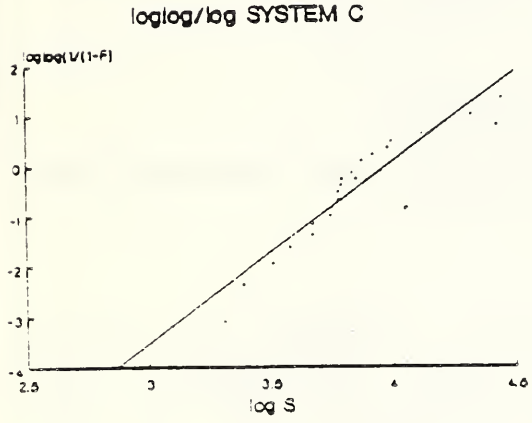

Fig. 1C

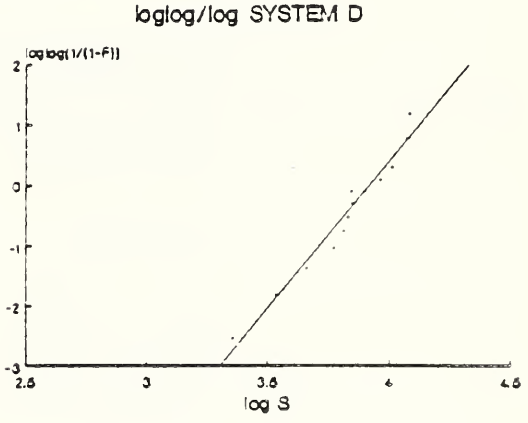

Fig. 1D

Loglog (1/1-F) vs log S for four dental porcelain-metal systems. F is the probability of failure at a stress S.

Table 1

Treatment	α^*	S^{*1} (Mpa)	S^{*2} (MPa)	m_1^*	m_2^*
Ethanol	0.63	50.8	52.4	5.6	19.2
Water	0.52	58.3	54.6	6.1	16.8
Heptane	0.49	52.0	50.2	6.1	10.8

It is interesting to note that the characteristic strength of the material does not change but only Weibull parameter. These results have been submitted to the World Congress on Biomaterials.

The weighting factor α is speculated to be linked to the immersion time in the particular liquid; for which $\alpha=0$ for $t=0$ and $\alpha=1$ for $t\to\infty$. This needs to be verified. The values for the weighting factor and its tentative explanation have been submitted to the IADR for inclusion in the 1988 General Session.

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

This effort is delayed to concentrate efforts on Weibull statistics related to dental material properties.

J. Metrology: Sterilization of Dental Implements

Feasibility of gas plasma sterilization of dental instruments and handpieces.

Overview

This study was designed to evaluate whether gas plasma sterilization is effective for dental instruments. The effectiveness of cold plasma sterilization or glow discharge sterilization has been demonstrated by R. Boucher.[5] The limitation on the further development of gas plasma sterilization has been the high power requirements for an RF generator that will sustain a plasma.

Part of the present study is to determine whether a commercially available microwave oven (of the household appliance variety) can be used as the RF source for the gas plasma. The optimum gas pressure (air or oxygen) for destruction of bacteria and spores is then to be determined.

PROGRESS REPORT

Accomplishments

Gas plasma ignition has been obtained in an evacuated chamber inside the microwave oven. Ignition occurs very readily and the oven appears to provide more than enough energy for the plasma. The modification and baffling of the microwave to permit a vacuum hose to enter the chamber during operations did not produce a measurable increase in the EM radiation around the unit. It was found that polycarbonate and polyprene materials show absorption of the EM radiation and are unusable as materials to construct the vacuum chamber. A new vacuum chamber has been designed, made of polyethylene that does not show this undesirable effect.

Phase I. Development of Plasmas

(a) Establish a vacuum chamber within the resonant cavity of the microwave oven.

(b) Produce a gas plasma with rapid ignition.

Phase II. Effects of Plasmas on Spores

Determine the optimum oxygen pressure and operating time to destroy Bacillus subtilis spores.

Phase III. Microashing Studies

Determine whether the plasma is of sufficient intensity to "microash" a virus. Microashing has been demonstrated by Frazier et al. [6]

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

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Okuno, O., Tesk, J., and Penn, R. Mesh Monitor Casting of Dental Alloys: Investment Effects. Cleared WERB review.

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Media Program, The Role and Future of Dental Materials, May 12, 1987.
Tesk, J.A. History of Dental Materials Research
Tesk, J.A. Recent Developments at NBS in Dental Materials

Invited Talks

de Rijk, W.G., Refractory Materials for Ceramic Processing. The Sixth International Symposium on Ceramic Processing. Los Angeles, CA June 21, 1987

de Rijk, W.G., Porcelain Metal System Strength and Weibull Modulus and Characteristic Strength. Engineering Foundation Conference on Applications of Modern Engineering Methods to the Design/Fabrication of Dental Prostheses. Henniker, NH July 16, 1987.

Tesk, J.A. How can you design a dental material? Johns Hopkins University, March 1987.

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5. AUTHOR(S) J. Tesk, G. Brauer, J. Antonucci, J. McKinney, J. Stansbury, S. Venz, S.Lee, W. de Rijk, R. Penn, A. Sugawara, K. Asaoka

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

12.

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