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Properties and Interactions of Oral Structures and Restorative Materials

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National Institute of Standards and Technology
(Formerly National Bureau of Standards)
Institute for Materials Science and Engineering
Polymers Division
Dental and Medical Materials
Gaithersburg, MD 20899

Annual Report for Period

October 1, 1987 to September 30, 1988

Issued May 1989
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Prepared for:
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National Bureau of Standards became the
National Institute of Standards and Technology
on August 23, 1988, when the Omnibus Trade and
Competitiveness Act was signed. NIST retains
all NBS functions. Its new programs will encourage
improved use of technology by U.S. industry.

Prepared for:
National Institute of Dental Research
Bethesda, MD 20892

U.S. DEPARTMENT OF COMMERCE
Robert Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Raymond G. Kammer, Acting Director

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ABSTRACT

The research program described herein is designed to achieve a number of objectives leading to improved dental restorative materials, techniques and applications of dental materials science for improved dental health care in general. Some of the research in dental composites is directed toward developing generic polymer science potentially useful for composite applications, e.g., durable resin matrices and stronger more durable coupling between fillers and resins. Improved reinforcement is sought by defining the type, and percentages of fillers which will result in improved performance of composites. Methods for reducing polymerization shrinkage and attendant stress and marginal leakage are also explored. Cements are investigated and basic formulations developed for lower solubility, higher biocompatibility, higher strength, greater toughness and adhesion to various substrates including enamel and dentin. Analysis techniques include IR spectroscopy, chromatography, x-ray analysis, mechanical testing, and dilatometry. Another major effort is directed at elucidating the fundamentals involved in wear and degradation of dental composites and restoratives. Wear and hardness measurement techniques are 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 88 SIGNIFICANT ACCOMPLISHMENTS

- A new class of difunctional monomers which can cyclize during polymerization has been developed for use in dental composite formulations. The resulting homopolymers exhibit high elastic moduli and extremely low levels of residual unsaturation.

- A spiro orthocarbonate monomer designed to maximize double ring opening under near ambient polymerization conditions was prepared. Initial results indicate that the free radical polymerization occurs exclusively by the ring opening mechanism which leads to volumetric expansion.

- A series of substituted α-methylene lactone monomers was synthesized and polymerized. The degree of solvent resistance in the resulting non-crosslinked homopolymers was related to the various substituents. In general, solvent resistance was excellent.

- Several types of resin-modified glass-ionomer cements were developed which yield tough, more hydrolytically resistant hybrid cement composites.

- For at least one composite resin it was demonstrated that after chemical degradation the diametral tensile strength values are described by a time dependent mixed Weibull distribution.

- A prediction on the service life of resin bonded dental restorations was made by treating clinical data as censored data in a Weibull distribution of failure times.

- With a microwave sustained gas plasma, spores of Bacillus subtilus were inactivated after an exposure time of 30 seconds.

- The stresses developed in a porcelain-metal slab were calculated by computer simulation.

- Ultrasonic measurements of two model dental composites showed that Poisson's ratio is not affected by the use of filler-resin coupling agents. This can be interpreted as evidence of residual radial compressive stresses around the filler particles.

- Completion of in vitro wear testing and environmental resistance of a fluorinated flexible-resin composite. This material had higher environmental resistance to intraoral fluids, but lower wear resistance than conventional composites.

- Completion of in vitro wear testing and environmental resistance of a hybrid cement-composite. This material, comprising a glass-ionomer cement and polymerized water-soluble monomer, displayed good wear resistance and complete absence of brittle fracture during wear customary for conventional glass-ionomer cements.

- Effect of topical fluoride-gel treatments on a commercial-radiopaque composite revealed a significant weight loss from successive treatments in topical fluoride gels, but no significant change in wear resistance.

- *In vitro* wear tests of human enamel against a commercial castable-ceramic restorative revealed enhanced wear of enamel when a staining glaze was applied (as recommended by the manufacture) to the ceramic.

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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 prostheses or for their use as intermediate restoratives.

Non-eugenol containing cements based on vanillate esters, o-ethoxybenzoic acid (EBA) and zinc oxide, have been developed in this laboratory [1-7][1]. These cements have the following advantages compared to the presently used Zinc Oxide-Eugenol (ZOE) or EBA cements: (1) excellent strength, (2) much lower solubility than zinc oxide-eugenol cements, (3) do not inhibit free radical polymerization and can be used in conjunction with composite filling materials to which they adhere, 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 of their mechanical properties; (4) synthesis of cements containing the potentially caries-reducing syringic esters and

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

evaluation of properties of the resulting cements; (5) modification of the cements by addition of small concentrations of additives such as acids, metals or fluorides to improve their properties and (6) furnish assistance and guidance to conduct investigations of the biocompatibility and toxicity of the cement and its ingredients and collaborate in studies of the pulp irritation and in clinical studies at various dental research centers.

Accomplishments

Objectives 1 - 5 have been completed. Results of these studies have been summarized in References 1-16 and in the previous reports. These investigations have led to a number of cements and intermediate restoratives of potentially great usefulness for clinical dentistry.

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

PROGRESS REPORT

Phase I. Further Improvement of Properties of Vanillate and Related Cements

Because of the emphasis placed on other portions of research conducted under this interagency agreement, no studies were carried out on this phase during the year.

Phase II. New Applications of These Materials

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

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

(1) Biocompatibility

Past Accomplishments

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

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

Progress

(a) Biological Evaluation of Zinc Hexyl Vanillate Cements

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

(b) Biological Evaluation of Vanillate Intermediate Restoratives.

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

(2) Assistance in Clinical Evaluation

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

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

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B. Changes in Esthetic Properties of Dental Resins on Aging

Overview

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

Objective

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

Accomplishments

The color stability of composites on exposure to irradiation by (1) Xenon lamp, (2) a standard RS light source and (3) elevated temperature at 60°C, in air or water and under different experimental conditions for various time periods were investigated. Composites studied included chemically and light cured hybrid and microfilled resins and a material copolymerized by light and chemical aftercure. Color changes of composites intensified on increasing the irradiation time. Exposure to the light sources under similar conditions gave comparable results. Visible light cured materials were more color stable than two common chemically cured composites. Light shades yielded more visible color changes than dark shades of the same brand. There was a significantly more severe discoloration of composites kept in water at 60°C than for those stored in air. Comparison with results in two clinical studies of color changes using two of the chemically cured composites investigated here, indicates that these restoratives, which pass the ANSI/ADA and the ISO specification tests, discolor in clinical use after 2-3 years.

Because of the intense discoloration which had occurred, quantitative estimation of the color changes which took place after one year water storage proved difficult.

Analytical high pressure liquid chromatography identified the major constituents of composite pastes.

A recently published manuscript [1] of this work 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.

PROGRESS REPORT

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

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

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

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

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C. Development of Radiopaque Copolymeric Denture Resins

Overview

The ever increasing use of plastics in dentistry makes it desirable and often mandatory that the materials have adequate radiopacity to detect their presence in various environments [1]. Radiopacity is an important requirement for medical and dental implants or devices that may be ingested accidentally. The commonly available high molecular weight plastics are composed of elements of low atomic number. The low cross-sectional electron density of the polymer chain makes them radiolucent to x-ray imaging techniques. Attempts to render plastics radiopaque have taken the following approaches: (1) incorporation of radiopaque metals such a lead foil, gold or silver alloy [2-4], (2) addition of heavy metal salts such as barium sulfate, barium acrylate, bismuth subnitrate or yttrium fluoride as fillers [5-8], or (3) incorporation of an element of high atomic number into a silanized glass used as reinforcing filler of a composite resin [9-12], (4) addition of halogenated saturated or unsaturated compounds such as tetrabromoethane or aliphatic bromoacrylates or methacrylates to the uncured resin [13,14]. Permanent radiopacity can also be achieved by entrapping polymer salt complexes such as those prepared on chelating copolymers of methyl methacrylate with $BaBr_2$ to produce polymer salt complexes in an interpenetrating poly (methyl methacrylate) network [15,16]. All these modifications have certain disadvantages. Addition of metal or metal salts causes stress concentrations at the interface between the insert and the resin which will weaken the materials. It also lowers the mechanical properties (transverse, impact, compressive and tensile strength). Translucency of such radiopaque plastics is usually lower than those containing no additives. Plastics with radiopaque glass ingredients are difficult to polish. Resins with halogenated aliphatic ingredients discolor with time and are unsuitable for many applications where esthetic characteristics are important. The presence of aromatic monomers in the polymerizable paste greatly reduces the storage stability of such mixtures.

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.

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

PROGRESS REPORT

Phase I. Using Commonly Accepted Testing Procedures, Study the Curing Characteristics and the Physical, Chemical, Esthetic and the Radiopaque Properties of Self-Curing Denture Base Materials Prepared from Copolymers of Pentabromophenyl- and Triiodophenyl Methacrylate and Methyl Methacrylate Copolymers.

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

Phase II. If the Properties of Formulation Studied in Phase I Pass all Requirements of the ANSI/ADA Specification for Denture Base Resins, have Adequate Working Properties and Good Esthetic Characteristics, We will Determine the Biocompatibility of the Added Monomer and of the Cured Denture Base Copolymer Resin.

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

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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. Acid pretreatment of enamel 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]. Major disadvantages of the dentin bonding systems are (1) the tooth surface must undergo a number of pretreatments which are time-consuming and may limit the 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].

Two difunctional monomers, m-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) and 2-isocyanatoethyl methacrylate (IEM) and 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, or $-NH_2$ of the amino acids present in collagen, yielding covalent bonds with the tissue surface. The resulting adduct possesses -C = C- 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 serve as adhesives or sealants and to synthesize compounds and formulations containing functional groups that are effective adhesion promoters to mineralized tissues. Specifically these studies will (1) determine the grafting efficiency of oligomers and polymers of TMI or IEM and methacrylate with pendant isocyanate groups with the aim of obtaining a durable adhesive bond to 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) with pendant isocyanate groups have been synthesized from m-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) and/or 2-isocyanatoethyl methacrylate (IEM), two difunctional monomers (Fig. 1) and over 50 methacrylate or vinyl monomers. The compounds were characterized by physico-chemical means. Most of the oligomers are liquids at room temperature, stable in air, have a MW range from 1400 to 2600 and an isocyanate content from 5% to 18%. Dilute solutions of the compounds, especially those with TMI or IEM and TMI and methacrylate constituents yielded stronger, more permanent bonds to glutaraldehyde treated bone than other tissue adhesives. Thermocycling in water for one week between 5°C and 55°C did not decrease adhesion indicating that exposure to water or thermal shock produced no deterioration of the bond. No correlation between bonding efficiency and -NCO content or increase in molecular weight could be established. Tensile adhesion of human dentin joined to composite restorative resins by means of the oligomers was similar to that of the best dental bonding agents. Vinyl monomers containing oligomers are preferable to bond dentin to dental composites. The oligomeric compositions are also excellent tissue adhesives and provide a strong bond between collagenous substrates such as calfskin and cured denture base resins.

PROGRESS REPORT

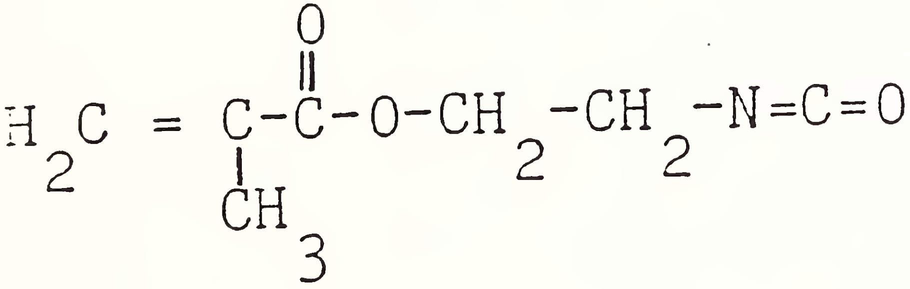
Phase Ia. Synthesize and Characterize Oligomers with Pendant Isocyanate Groups.

Fig. 2 shows the structure of typical oligomers synthesized in this study.

A series of over 20 new methacrylate oligomers containing pendant isocyanate groups were synthesized by reacting TMI and/or IEM in ethoxyethyl acetate with vinyl monomers such as vinyl acetate, vinyl stearate, 5-vinyl-2-norbornene, N-vinyl-2-pyrollidone or α-methylstyrene.

Table 1 lists representative oligomers synthesized, abbreviations used, ratio of monomeric reactants, 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 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 of selected oligomers indicated a molecular weight range from 1400 to 2600. The synthesis of compounds with higher molecular weight was accomplished by reacting the respective monomers at lower temperatures (60°C) for longer periods of time (48 to 60 hours) and using smaller quantities of AIBN initiators than previously employed. The resulting compounds had higher intrinsic viscosities (indicative of higher molecular weight) ranging from 0.05 dl/g for TMI-SMA to 0.14 dl/g for TMI-BMA as compared to the intrinsic viscosities of 0.024 to 0.036 dl/g for the oligomer obtained with reaction temperatures of 140°C. The higher molecular weight materials had a slightly higher isocyanate content.

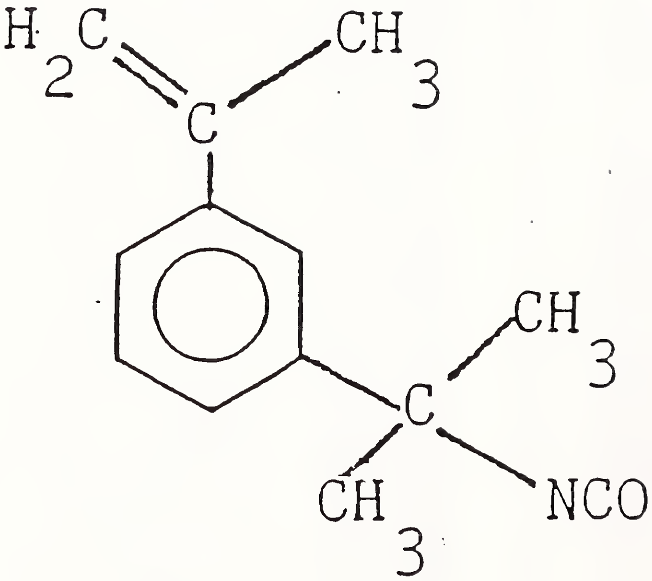
MONOMERS WITH ISOCYANATO GROUPS



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

2-Isocyanatoethyl methacrylate

IEM

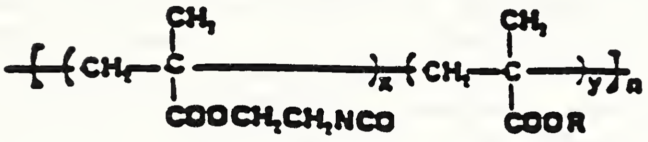


m-Isopropenyl-α,α-dimethylbenzyl Isocyanate

m-TMI

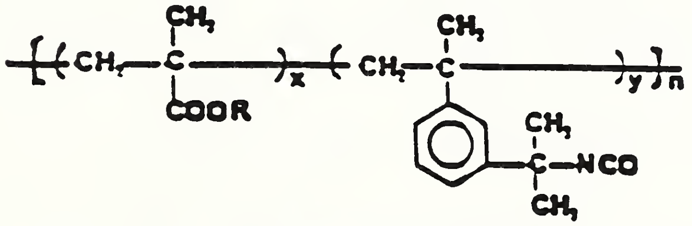
FIGURE 2

IDEALIZED STRUCTURES OF ADHESIVE OLIGOMERS

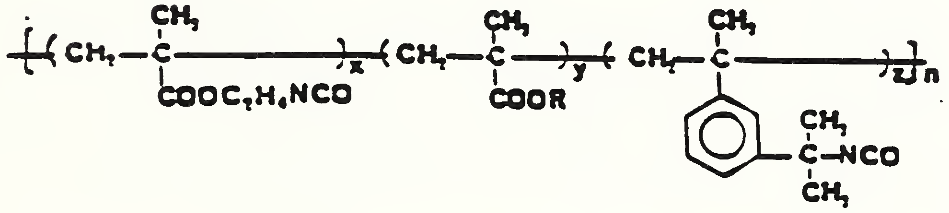


$$-\!\left[\left(CH_2-\overset{CH_3}{\underset{COOCH_2CH_2NCO}{C}}\right)_x\left(CH_2-\overset{CH_3}{\underset{COOR}{C}}\right)_y\right]_n$$

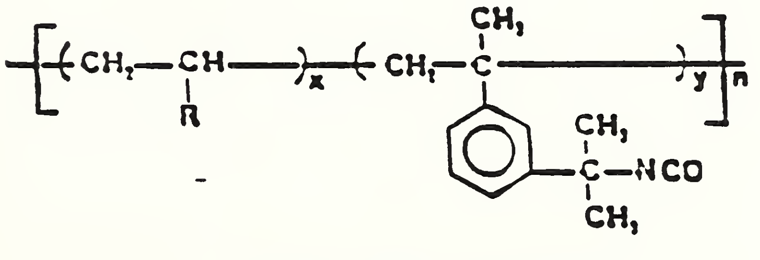
IEM - Methacrylate Ester



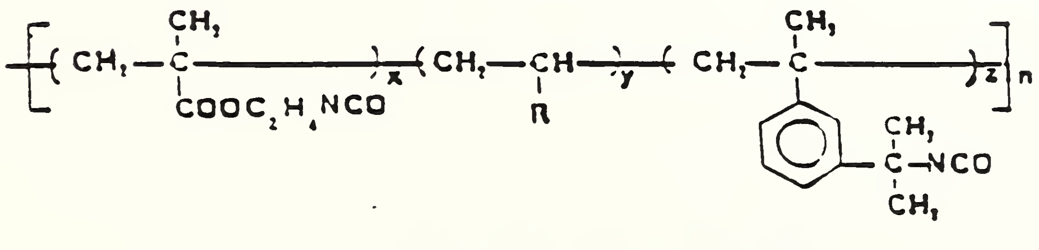
TMI-Methacrylate Ester



IEM-Methacrylate Ester-TMI



TMI-VINYL MONOMER



IEM-VINYL MONOMER-TMI

Isocyanate groups determined titrimetrically or spectrophotometrically ranged from 5% to 18% per molecule. The spectrophotometric procedure to determine the isocyanate content of compounds developed by us depends on the intensity of the infrared absorption peak between 2251 cm^{-1} and 2267 cm^{-1}. It is much more rapid than the conventional titrimetric technique. As shown in Table 2 results of both procedures are in good agreement. The observed percentage of -NCO groups of many oligomers is considerably lower than the theoretical amount, i.e. the calculated value, assuming complete conversion of monomers to the oligomers. 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. A manuscript describing the synthesis and characterization of the oligomers has been accepted for publication in the J. Biomed Mater. Research.

Phase Ib. Prepare Adhesive Formulations and Evaluate Their Properties.

The tensile bond strengths of glutaraldehyde treated bovine bone cemented with various oligomers (synthesized in phase Ia) are summarized in Table 3. Highest bond strength was obtained with adhesive formulations of IEM (9.9 MPa) and TMI (9.0 MPa) monomers, followed by those containing IEM-BMA-TMI and IEM-CHMA-TMI (8.5 MPa) with 17 other oligomers fracturing above an applied load of 6 MPa. Bond strength values between 9.9 MPa and 6.8 MPa are not statistically significantly different ($p<0.05$). After 7-day thermocycling between 5°C and 55°C the joints cemented with IEM or TMI monomer showed a slight decrease in bond strength whereas six of the nine oligomers studied had a slightly improved adhesion.

TABLE 1

PROPERTIES OF IEM-METHACRYLATES (OR VINYL)-TMI OLIGOMERS SYNTHESIZED

Monomeric components:[a]	Abbreviation	n_D^{23}	%NCO	
			Found[b]	Calcd
IEM-Methacrylate (ma) Esters				
" - butyl ma	IEM-BMA	1.477	9.58	14.27
" - i-bornyl ma	IEM-BOMA	1.485	6.33	11.12
" - dicyclopentenyloxethyl ma	IEM-QM	1.505	7.31	10.13
TMI-Methacrylate Esters (ma)				
" - butyl ma (1:1.4)	TMI-BMA(1:1.4)	1.514	12.15	10.49
" - stearyl ma	TMI-SMA	1.481	6.11	7.78
IEM-Methacrylate Esters (ma)-TMI				
" - IEM-butyl ma-TMI (1.3:1.4:1)	IEM-BMA-TMI (1.3:1.4:1)	1.508	14.06	13.95
" - stearyl ma-TMI	IEM-SMA-TMI	1.485	8.64	12.08
" - allyl ma-TMI	IEM-AMA-TMI	1.515	14.84	17.40
" - cyclohexyl ma-TMI	IEM-CHMA-TMI	1.512	13.49	16.01
" - glycidyl ma-TMI	IEM-GMA-TMI	1.513	10.92	16.85
" - i-bornyl ma-TMI	IEM-BOMA-TMI	1.499	10.64	14.51
" - dicylopentenyloxyethyl-ma-TMI	IEM-QM-TMI	1.524	9.54	13.57
" - 9-vinylcarbazole-TMI	IEM-VC-TMI	1.563	16.27	15.28
" - styrene-TMI	IEM-S-TMI	1.538	14.64	18.23
" - α-methylstyrene-TMI	IEM-MS-TMI	1.526	13.65	17.70
" - vinyltoluene-TMI	IEM-VT-TMI	1.536	16.09	17.70
TMI-Vinyl Monomer				
TMI- vinyl acetate (1:2)	TMI-VAc	1.526	16.42	11.24
" - vinyl stearate	TMI-VS	1.478	5.73	8.21
" - vinyl butyl ether	TMI-VBE	1.525	16.22	13.93
" - 5-vinyl-2-norbornene	TMI-VNB	1.533	13.80	13.06
" - 1-vinylimidazole	TMI-VI	1.533	12.78	14.22
" - α-methylstyrene	TMI-MS	1.527	12.97	13.15
IEM-Vinyl monomer-TMI				
IEM - vinyl acetate-TMI	IEM-VAc-TMI	1.511	17.90	18.98
" - vinyl stearate-TMI	IEM-VS-TMI	1.481	8.46	12.59
" - 5-vinyl-2-norbornene-TMI	IEM-VNB-TMI	1.527	14.58	17.62
" - N-vinyl-2-pyrollidone-TMI	IEM-VP-TMI	1/531	16.33	17.96

---

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

[b] Determined tirimetrically.

TABLE 2

ISOCYANATE CONTENT OF SOME OLIGOMERS

	-NCO CONTENT, %		
OLIGOMER	FOUND		CALCD
	Titrimetric	Infrared	
TMI-ETHYL MA	13.16	13.46	13.32
" -STEARYL MA	6.11	6.05	7.78
"-VINYLNORBORNENE	13.80	13.30	13.06
"-VINYL ACETATE[a]	16.42	16.21	11.24
IEM-BUTYL MA-TMI[b]	14.05	13.70	13.95
"-STEARYL MA-TMI	8.64	8.78	12.08
"-CYCLOHEXYL MA-TMI	13.49	13.69	16.01

[a] Monomer ratio 1:2 [b] Monomer ratio 1.3:1.4:1

Thus, exposure to water and thermal shock produced no deterioration of the bond compared to the loss in bond strength experienced with 2-cyanoacrylate adhesives (8). All of the tensile strength specimens employed broke cohesively, with many fracturing within the bone. Generally, oligomers containing TMI or TMI and IEM and methacrylate ester constituents adhere more strongly to bone than those synthesized from IEM or vinyl monomers. Bonding to bone is strongest with methacrylate oligomers with high MW ester groups. From the experimental data no correlation between bonding efficiency and isocyanate content of oligomer could be established (Table 4). Oligomeric adhesives with intrinsic viscosity values ranging from 0.05 to 0.14 dl/g bond at least as well as to bone than the lower molecular weight materials. These studies are summarized in Table 5. Thus, the values for the bone to bone tensile adhesion of all five recently synthesized adhesives (IEM-BMA-TMI, IEM-MS-TMI, TMI-BMA, TMI-QM and TMI-SMA) were slightly, although not significantly, higher than those of similar oligomers of lower molecular weight.

The concentration or pH of the glutaraldehyde solution employed in the pretreatment of the bone did not influence greatly the strength of the bone joint. On varying the concentration of the glutaraldehyde solution between 5% and 25% (Table 6) or changing its pH between 3 and 9 (Table 7) no significant change ($p<0.05$) in the bond strength of bone specimens cemented together with TMI-BMA or IEM-BMA-TMI occurred.

TABLE 3

TENSILE BOND STRENGTH OF HUMAN DENTIN OR BONE JOINED WITH ADHESIVE OLIGOMERS

Monomeric Components: 2-Isocyanatoethyl methacrylate (IEM), methacrylate or vinyl monomer and/or m-isopropenyl-α,α-dimethylbenzyl isocyanate

	Bond Strength of Joint Cemented with Oligomer MPa		
	Bone to Bone[b]		Dentin to composite[c]
Adhesive[a]	24 h in H_2O	7d thermocycled[d]	24 h in H_2O
IEM	9.9 ± 1.4	-	6.4 ± 2.4
TMI	9.0 ± 1.8	-	4.3 ± 1.1
IEM-BMA	6.9 ± 2.0	7.5 ± 1.6	4.4 ± 1.7
IEM-BOMA	2.8 ± 1.1	-	3.9 ± 1.4
IEM-QM	5.2 ± 1.9	-	6.3 ± 3.0
TMI-BMA(1:1.4)	7.7 ± 1.1	7.9 ± 1.7	3.6 ± 1.1
TMI-SMA	7.5 ± 1.3	8.7 ± 1.5	3.9 ± 1.3
IEM-BMA-TMI(1.3:1.4:1)	8.5 ± 2.2	7.4 ± 1.6	3.9 ± 1.6
IEM-SMA-TMI	7.4 ± 1.5	8.1 ± 1.8	4.5 ± 2.4
IEM-AMA-TMI	6.8 ± 2.3	6.7 ± 1.5	4.9 ± 2.2
IEM-CHMA-TMI	8.4 ± 2.6	8.2 ± 1.4	2.3 ± 0.9
IEM-GMA-TMI	4.7 ± 2.0	-	5.4 ± 2.6
IEM-BOMA-TMI	7.0 ± 3.1	7.2 ± 1.5	3.3 ± 1.6
IEM-QM-TMI	7.5 ± 3.0	8.4 ± 1.5	3.8 ± 1.3
TMI-VAc(1:2)	5.4 ± 1.9	-	5.4 ± 1.7
TMI-VS	6.8 ± 3.0	-	3.1 ± 1.6
TMI-VNB	6.5 ± 2.6	-	5.5 ± 1.8
TMI-VI	4.6 ± 1.6	-	4.2 ± 1.2
TMI-MS	6.1 ± 1.6	-	5.4 ± 2.0
IEM-VAc-TMI	6.8 ± 1.0		5.2 ± 1.6
IEM-VNB-TMI	6.3 ± 1.5	-	5.8 ± 2.2
IEM-VP-TMI	5.5 ± 0.8	-	5.2 ± 1.4
IEM-VC-TMI	5.4 ± 2.0	-	4.8 ± 2.0
IEM-S-TMI	5.2 ± 1.8	-	4.5 ± 1.4
IEM-MS-TMI	6.6 ± 1.6	-	5.7 ± 1.6
IEM-VT-TMI	6.3 ± 0.6	-	4.3 ± 1.1
GLUMA[e]	7.1 ± 0.8	6.9 ± 1.4	4.2 ± 2.7
NPG-PMDM[f]	3.0 ± 1.5	-	3.3 ± 2.0
Control[g]	1.1 ± 0.6	0.3 ± 0.3	

[a] For abbreviations refer to Table 1.

[b] Procedure of Brauer et al (3), Bone was treated with 5% aq. glutaraldehyde. A 5% solution of the adhesive in CH_2Cl^2 was applied, followed by application of bonding resin. Mean of 10 specimens ± standard deviation.

[c] Procedure of Lacefield et al (29) was used. Dentin was pretreated with 0.5M EDTA and 5% aq. glutaraldehyde. A 5% solution of the adhesive in CH_2Cl was applied, followed by application of a bonding resin and composite. Mean of 5 specimens ± standard deviation

[d] Between 5°C and 55°C-540 cycles per day.

[e] Glutaraldehyde-2-hydroxyethyl methacrylate-following EDTA pretreatment.

[f] Ferric oxalate + N-phenylglycine + dimethacryloxyethyl pyromellitate.

[g] Adhesive

Oligomers with pendant -NCO groups prepared from TMI or IEM-TMI and vinyl monomers are more effective adhesives for cementing dentin to composites than those synthesized with methacrylate esters (Table 3). Dentin cemented to composite with IEM-VNB-TMI, IEM-MS-TMI, TMI-VNB, TMI-VAc or TMI-MS had bond strength varying from 5.4 to 5.8 MPa. These values were higher than those for oligomeric adhesives with methacrylate ester as constituents. Two other bonding agents suggested for dentin, Gluma and NPG-PMDM, had bond strength of 4.2 MPa and 3.4 MPa respectively. Presence of heterocyclic nitrogen containing vinyl monomers in the oligomeric adhesive did not improve bonding. Analogous to the results obtained for bone, increase in the molecular weight of the oligomers slightly improved bonding to dentin (Table 5).

The oligomeric adhesives also bond well to soft tissues. Thus, two calfskin specimen joined together with TMI-BMA, after standing in air for 24 h, fractured only after application of a 25.0 kg load. On exposure to H_2O, the calfskin swelled causing a rapid loss of tear strength which made accurate bond strength determinations impossible. However, these bonded specimens stayed intact on storage in water over a six month observation period. Calfskin cemented to acrylic denture resins with IEM-VT-TMI or 8 other oligomers, when tested after 24 h storage in air, broke after applying a load in excess of 20 kg, with some of the specimens fracturing within the denture base. The results are given in Table 8.

TABLE 4

EFFECT OF ISOCYANATE CONTENT OF ADHESIVE ON BOND STRENGTH

OLIGOMER	-NCO CONTENT	BOND STRENGTH BONE	DENTIN
	%	MPa	MPa
TMI-VS	5.5	6.8	3.1
IEM-SMA-TMI	8.7	7.4	4.5
IEM-BMA(1:1.4)	12.0	7.7	3.6
TMI-MS	12.8	6.1	5.4
IEM-BMA-TMI[a]	13.9	8.5	3.9
IEM-VNB-TMI	14.6	6.3	5.8
IEM-VAc-TMI	17.1	6.8	5.2

---

[a] Monomer ratio 1.3:1.4:1

TABLE 5

EFFECT OF MW OF ADHESIVE ON BOND STRENGTH

OLIGOMER	INTRINSIC VISCOSITY	TENSILE ADHESION TO BONE	DENTIN
	dl/g	MPa	MPa
TMI-BMA[a]	0.069	7.0 ± 1.5	3.8 ± 0.8
" "	0.14	7.3 ± 1.8	4.1 ± 1.1
TMI-QM	0.039	6.3 ± 2.0	4.5 ± 1.1
" "	0.10	6.4 ± 2.0	4.8 ± 1.0
IEM-MS-TMI	0.021	6.2 ± 1.8	5.2 ± 1.2
" " "	0.11	6.3 ± 1.9	5.6 ± 2.1
IEM-BMA-TMI[b]	0.064	8.1 ± 2.0	4.2 ± 1.5
" " "	0.13	8.3 ± 2.1	4.3 ± 1.4

---

[a] Monomer ratio 1:1 [b] Monomer ratio 1.3:1.4:1

TABLE 6

EFFECT OF CONCENTRATION OF GLUTARALDEHYDE ON ADHESION TO BONE

OLIGOMERIC ADHESIVE: 5% IEM-BMA-TMI

CONC. OF AQ. GLUTARALDEHYDE	BOND STRENGTH TENSILE	SHEAR
	MPa	KG
1%	-	19
5%	8.5 ± 2.2	41
25%	8.7 ± 1.5	43

TABLE 7

EFFECT OF pH OF GLUTARALDEHYDE ON ADHESION TO BONE

CONCENTRATION OF AQ. GLUTARALDEHYDE: 5%

pH OF GLUTAR-ALDEHYDE	BOND STRENGTH[a] OF BONE CEMENTED WITH TMI-BMA	IEM-BMA-TMI
	MPa	MPa
3	6.6 ± 1.6	6.5 ± 2.3
5	7.0 ± 1.4	7.9 ± 1.8
7	6.9 ± 1.6	8.0 ± 1.8
9	5.9 ± 1.9	6.3 ± 1.9

[a] Mean of 10 determinations

Three talks were presented discussing these studies. A manuscript summarizing this research has been published, another manuscript "Oligomers with Pendant Isocyanate Groups as Tissue Adhesives II. Adhesion to Bone and Other Tissues" has been accepted by the J. Biomed Mat Research. Two other papers have been submitted for publication. A patent for these adhesive oligomers has been applied for.

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 is being studied at Northwestern University, the Medical College of South Carolina and the Dental School, University of Regensburg, Germany, Dept. of Orthopaedics, University of Calgary, Canada and the University of Liverpool, England. Over 300 bone specimens cemented with the three oligomers have been prepared and were implanted by Dr. Kafrawy at the University of Indiana to study tissue reactions of the cured adhesive. Feasibility of using these materials as soft tissue adhesives is being explored at the Ohio State School of Dentistry.

Studies conducted by Dr. Schmalz, University of Regensburg indicate that the undiluted oligomers containing IEM are cytotoxic whereas those with TMI show only very moderate cytotoxicity. Based on these results different TMI monomers that should have minimum cytotoxicity have been prepared and sent for evaluation.

TABLE 8

Relative Adhesive Shear Strength of Soft Tissue (Calfskin) Cemented to Cured Denture Base with Oligomers

Specimens stored in air for 24h

Oligomeric Adhesive*	Load at Fracture in kg†
TMI-SMA	18.16 ± 4.71
TMI-VS	21.09 ± 6.57
IEM-BMA-TMI(1.3:1.4:1)	23.70 ± 5.87
IEM-CHMA-TMI	22.44 ± 8.92
IEM-VAc-TMI	15.67 ± 5.82‡
IEM-VS-TMI	20.15 ± 5.26‡
IEM-VBE-TMI	13.79 ± 6.51‡
IEM-VNB-TMI	20.36 ± 4.72
IEM-VP-TMI	17.18 ± 5.15‡
IEM-VC-TMI	18.97 ± 4.71‡
IEM-S-TMI	14.69 ± 2.25‡
IEM-MS-TMI	21.50 ± 3.48
IEM-VT-TMI	25.62 ± 5.03

* For abbreviations refer to Table 1
† Mean of 10 determinations ± standard deviation
‡ Mean of 5 determinations ± standard deviation

Recent studies have shown that oligomers with lower isocyanate content or higher molecular weight than those originally prepared have the same adhesive properties as the oligomers initially synthesized. The higher MW compounds have lower volatility and boiling points, should diffuse more slowly into tissues and may have lower irritational properties.

The adhesives described in this study comprise a generic series of oligomers. Thus, 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 obtain molecules having the desired physical, chemical and biological properties or to modify, if necessary, any adverse tissue reactions. Subject to their acceptable biocompatibility these oligomers could find applications in medical, dental or veterinary procedures.

Phase II. Synthesize the Dimethacrylate Ester of 5-(2,5-Dioxotetra-Hydrofuryl)-3-Methyl-3-Cylohexene-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 viscous product adhered well to ferric oxalate treated bone and composite. The bond strength appeared to be lower than that of the isocyanate 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.

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Contributed Talks

Brauer, G.M., and Lee, C.H. Properties of Oligomeric Adhesives with Pendant Isocyanate Groups. IADR, Montreal 1988.

Lee, C.H. and Brauer, G.M. Oligomeric Adhesives from Vinyl Monomers, 2-Isocyanatoethyl Methacrylate and TMI. IADR, Montreal 1988.

Brauer, G.M. and Lee, C.H. Oligomeric Adhesives from Vinyl Monomers with Pendant Isocyanate Groups. Midatlantic Regional Meeting, American Chemical Society, Millersville, PA 1988.

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E. Monomers That Polymerize with Expansion

Introduction

A trait universally shared by conventional monomers in use today is the volume contraction that accompanies their conversion to polymer. In dental composite applications, this polymerization shrinkage can result in a number of defects including marginal gaps, loss of adhesion and interfacial debonding of the filler. These adverse effects can be countered by employing spiro orthocarbonates as ingredients in formulations since these monomers are capable of double ring-opening polymerization to give an expansion in volume.

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

A spiro orthocarbonate monomer was synthesized which integrates all the advantageous elements discovered through previous work with simpler model compounds. This new monomer, 2-methylene-8,9-benzo-1,4,6,11-tetraoxaspiro [4.6] undecane (I), has reactivity comparable to acrylic monomers used in resin-based dental polymers by virtue of the direct substitution of oxygen on the double bond. The five-membered, unsaturated ring also promotes more efficient double ring opening during polymerization. The seven-membered ring component induces additional strain which contributes to ring cleavage and it also provides asymmetry to help minimize the melting point of the monomer. The aromatic group serves to stabilize the ring-opened radical and thus, it too encourages this process. Additionally, the aromatic ring raises the glass transition temperature of the resulting polymers and gives a UV and IR visible marker.

Phase II. Polymerization

The polymerization of monomer I has been conducted in bulk and in solution at several temperatures. Under all conditions, complete double ring opening has occurred. This is the first spiro orthocarbonate monomer able to provide efficient, low temperature ring opening by a free radical mechanism. This is obviously an advantage for a monomer being considered for a dental application. The combination of reactivity, ring opening efficiency and the relatively rigid structure of its polymers make I an excellent candidate monomer for minimizing polymerization shrinkage in dental resin systems. A calculation of polymerization expansion and the evaluation of I in resin formulations remains to be completed.

Phase III. Formulation

The storage stability of a previously prepared spiro monomer (II) which contains the unsaturated five-membered ring functionality was investigated in formulations activated for either light cure or chemical cure. The formulations were prepared by adding 25 wt.% of II to a control mixture comprised of ethoxylated bisphenol A dimethacrylate and hexamethylene glycol dimethacrylate (9:1). The ^{1}H and ^{13}C NMR spectra were taken immediately after mixing the experimental formulations. These were compared with the analogous spectra obtained after four months of room temperature storage. There was no indication of significant change in any of the components. This relatively hydrophobic resin was chosen to minimize the potential for hydrolysis of the spiro orthocarbonate. A parallel study involving II in conjunction with a more hydrophilic BIS-GMA/triethylene glycol dimethacrylate resin is currently underway.

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

Composites prepared from the formulations described in Section III provided cured materials with acceptable mechanical strength properties. The polymerization shrinkage results as well as adhesive properties of these formulations will be conducted in the near future.

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

This work awaits completion of Phase IV.

Invited Talks

Stansbury, J.W., and Bailey, W.J. Synthesis and Free Radical Polymerization of Unsaturated Spiro Orthocarbonates. Mid-Atlantic Regional Meeting of the American Chemical Society, High Performance Polymers Symposium, Lancaster, PA, May 1988.

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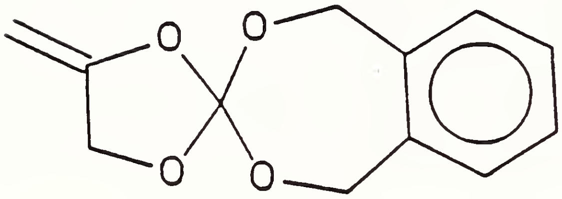

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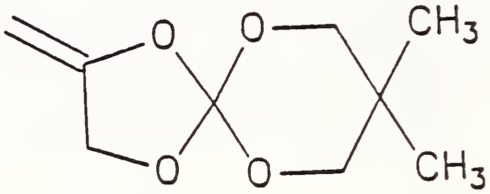


II

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 polar 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 oligomer and diluent multifunctional monomers of higher fluorine content, workable viscosities and greater flexibility.

This part of Phase I was deferred due to technical problems which affected the performance of the High Performance Liquid Chromatograph which is essential for establishing the purity and aiding in the characterization of monomers such as 2,2,3,3,4,4-hexafluoro-1,5-pentamethylene dimethacrylate [30].

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

There is evidence [17-20] that a significant, contributory factor involved in the failure of dental composites is the susceptibility of their polymeric matrices and interfacial phases to swelling and possible chemical degradation induced by oral fluids. Accordingly, it is important to develop polymeric systems which are highly resistant to intraoral fluids, which include organic components as well as the ubiquitous water. In order to improve the resistance to degradation from the intraoral environment, the dental polymer should have the following characteristics:

(1) a low solubility parameter

(2) a high glass transition temperature (T_g) as a result of a high degree of cure and crosslink density in the resin

(3) a low polymerization shrinkage

(4) and the ability to bond effectively to the filler phase via interfacial coupling agents and/or other modes interfacial attachment.

The following resin formulation was designed to optimize (1) (2) and (3). PFMA (Fig. 1) was blended with three diluent monomers, the bis(methacryloxyethyl) ether of resorcinol (MER), 1,10-decamethylene dimethacrylate (DMDMA) and α-methylene γ-butyrolactone, α-MBL, [36,37] shown in Fig. 2 along with a photoinitiator system consisting of camphorquinone (CQ) and ethyl 4-N,N-dimethylaminobenzoate (4EDMAB). The ingredients used in the formulation of these PFMA dual-cured materials (PFMA-DC) are listed in Table 1. The compositions of the PFMA-DC resin and composite are given in Tables 2 and 3, respectively. Both are two part systems. Mixing equal parts of resin 1 and resin 2 of Table 2 results in a conversion of 65% compared to 53% for the same resin system that is cured only by visible light initiated polymerization. The diametral tensile strengths of their corresponding composites was 46 and 39 MPa, respectively Knoop hardness determinations showed similar differences with the PFMA-DC composites having the higher values. A similar study was done with a commercial resin (NCO, Caulk/Dentsply) and its composites. The results indicate that the dual-cured resin had the higher conversion (77% vs 71%) and its corresponding composite the higher diametral tensile strength (59 vs 47 MPa) than usual light cured materials. Two papers based on these studies were presented at the 1988 IADR meeting.

(c) Synthesis of highly fluorinated multifunctional methacrylates based on hexachlorocyclophosphazene has been dropped due to similar work being done elsewhere [33-35].

(d) Silyl ether derivatives.

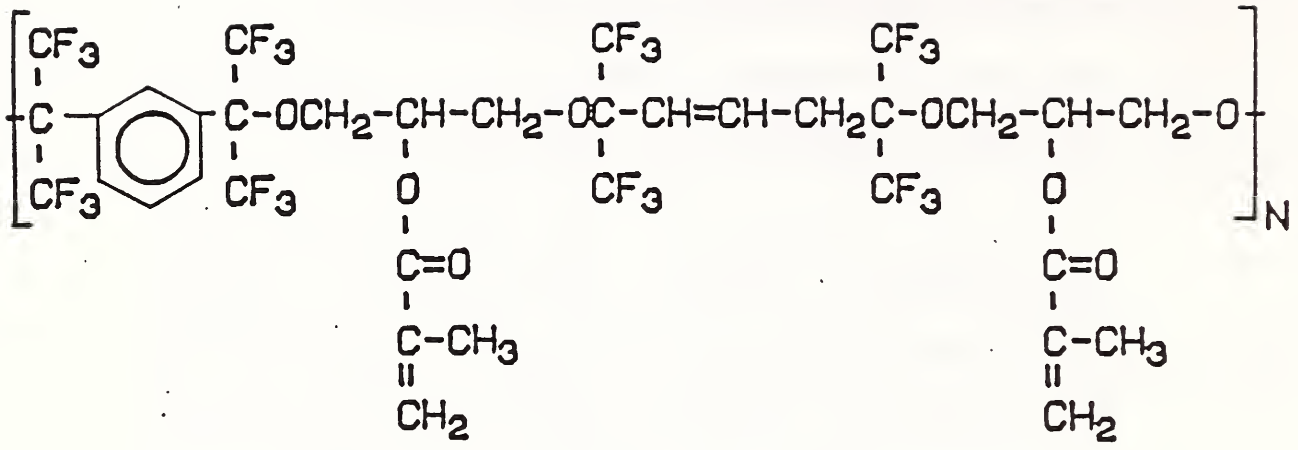
No work was done on this project in FY88.

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

No work was done on this project in FY88.

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

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



MW (Repeat) = 1032

Av. MW ≅ 10,320 (N ≅ 10)

Fig. 1. Chemical structure of the base oligomer PFMA.

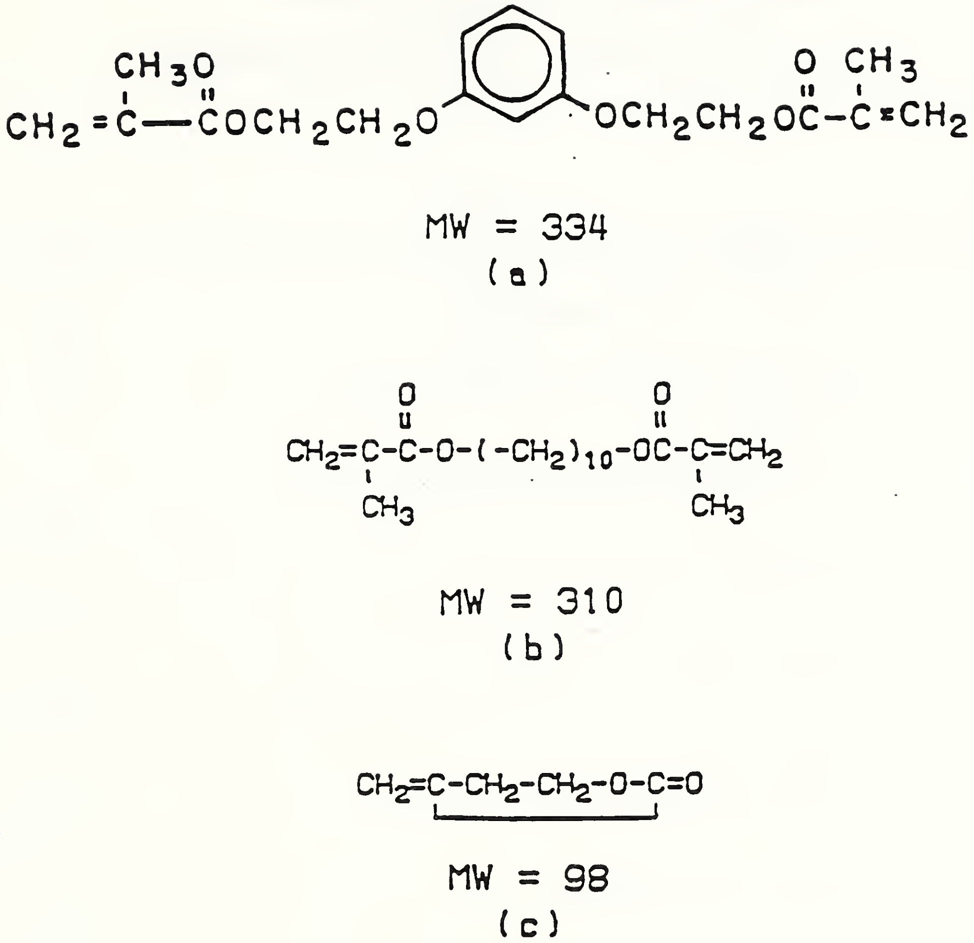


Fig. 2. Chemical structure of the diluent monomers used in the PFMA-DC resin. (a) MER, (b) DMDMA, and (c) α-MBL.

Table 1
Ingredients of the PFMA-DC Composite

Abbreviation	Name	Source
PFMA	Poly(fluoromethacrylate)	NBS
MER	1,3-bis(2'-methacryloxyethoxy) benzene	PRF* (ADA)-NBS
DMDMA	1,10 decamethylene dimethacrylate	Esschem Essington, PA
α-MBL	α-methylene-γ-butyrolactone	Aldrich Chemical Co. Milwaukee, WI
4EDMAB	ethyl 4-N,N,-dimethylaminobenzoate	Aldrich Chemical Co. Milwaukee, WI
CQ	Camphorquinone	Aldrich Chemical Co. Milwaukee, WI
BPO	Benzoyl peroxide	Lucidol/Penwalt Buffalo, NY
FFQ	Fine fused quartz	Caulk/Dentsply Milford, DE
A-174™	3-methacryloxypropyl-trimethoxysilane	Union Carbide New York, NY

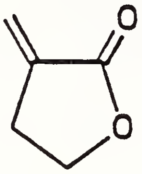
*Paffenbarger Research Foundation (American Dental Assoc.)

Table 2
Composition of the PFMA/DC Resin

Component	Resin 1 Wt. %	Resin 2 Wt. %
PFMA	68.57	68.55
MER	18.07	18.07
DMDMA	10.03	10.03
α-MBL	1.37	1.37
4EDMAB	1.56	-
CQ	0.40	-
BPO	-	1.98
Total	100.00	100.00

Resin 1/Resin 2 (wt/wt) = 1.00

This should yields monomers which can polymerize and crosslink to provide materials with high degrees of conversion and extreme resistance to chemical softening.



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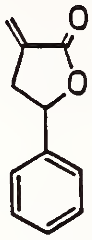
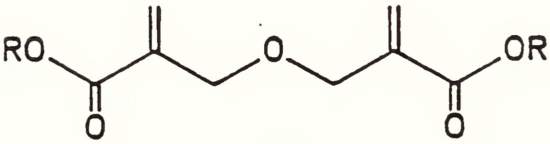


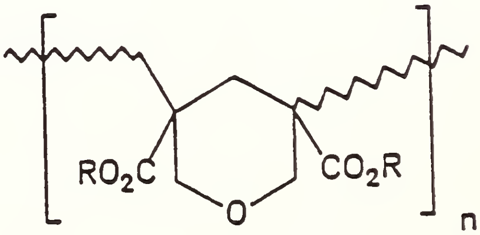
II

III

An outgrowth of the work on methylene lactones has lead to the formation of a new class of difunctional monomers (IV). The reaction between formaldehyde and conventional acrylate monomers gives a diacrylate with pendant ester groups which can be varied to alter properties of the monomer. The monomer (R=ethyl) obtained from ethyl acrylate can be used as a diluent comonomer while the bulkier monomer (R-phenethyl) based on phenethyl acrylate is better suited as a base monomer in resin formulations. Due to the position of the double bonds, these monomers can polymerize by a highly efficient cyclization process which introduces a six-membered ring into the polymer backbone (V). This mechanism allows polymerizations at near ambient conditions to proceed to high degrees of conversion (R=ethyl; 78%, R=phenethyl; 100%) while producing polymers containing rigid units which should convey good mechanical strength properties to materials incorporating these monomers.



IV



V

Table 3
Composition of the PFMA-DC Composite

Component	Wt.%
Resin:	
PFMA	69.25
MER	18.25
DMDMA	10.13
α-MBL	1.38
4EDMAB	0.79
CQ	0.20
Total Resin	100.00
Filler:	
FFQ	98.50
A-174	0.50
BPO	1.00
Total Filler	100.00

Filler/resin (wt/wt) = 2.20

(g) Improved initiator systems for dental resins

Several types of dual-curing initiator systems were investigated in an attempt to overcome the limited depth of cure of conventional visible light initiator systems based on camphorquinone and tertiary amines. Two part systems utilizing benzoyl peroxide as the chemical initiator yield better cured composites than the corresponding one part, visible light activated composite as previously described. Two part dual-curing systems suffer from the usual deficiencies of two component chemically activated resin systems; namely, limited working time and the introduction of porosity due to component mixing. It would be desirable to have a one component resin based dental material that possessed dual-cure characteristics, i.e. photochemical plus chemical initiating potential. The problem has been on how to stabilize such a system. In this study we explored the feasibility of using PFMA based resins (Fig. 1), which have the capability of dissolving more oxygen than conventional dental resins, as means of improving the storage stability of dual-curable, one-part resin based dental materials. BIS-GMA resins containing CQ, 4EDMAB and 1% b.w. BPO have poor storage stability at room temperature/about 30 minutes) With a PFMA resin the same initiator system did not cause gelation for 3-4 hours. The substitution of the more thermally stable peroxides such as t-butyl perbenzoate or cumene hydroperoxide improves the storage stability of both resin types towards premature gelation. Composites based on the PFMA resin shown in Table 2 containing, CQ(0.4%) and 4EDMAB (1.6%) and either t-butyl perbenzoate (2%) or cumene hydroperoxide (2%) had diametral tensile strengths of 43 and 45 MPa, respectively. With the resins containing CQ, 4EDMAB and cumene hydroperoxide, it was noted that visible light photoactivity decreased with time presumably due to the oxidation of CQ by the hydroperoxide since the resin was reactivated by the addition of CQ. It is not known at this time if a similar but slower degradation of CQ occurs with resins containing CQ and peresters. While this study did not result in a sufficiently stable, single paste, dual-curable composite, it did demonstrate that dual-cure initiator systems improve the conversion, uniformity of cure and related properties of resin based dental materials. A paper based on this work was presented at the 1988 IADR meeting.

II. Improvement of Dental Cements

Overview

Although used in relatively small quantities, dental cements are essential in a number of dental applications as: (a) temporary, intermediate and, in some cases, more permanent restoratives, (b) cavity liners and bases, (c) luting agents to bond preformed restorations and orthodontic devices, (d) pulp capping agents and endodontic sealers, and (e) impression pastes. This wide range of dental uses makes it virtually impossible for one type of cement to have all the necessary properties demanded in these diverse applications. Therefore, there is a need to develop "tailored" dental cements with certain optimal properties, especially biocompatibility, durability and adhesiveness. One approach for improving the overall properties of dental cements involves developing hybrid cement-composites or resin-modified cements. Of special interest are the glass ionomer cements, a class of relatively high modulus cements which adhere to enamel and, to a lesser extent, to dentin. With minimal surface preparation, adhesive strength is higher to enamel than dentin (presumably because of the lower mineral content of the latter), but the system is relatively weak in either case because of the low tensile and flexural strength inherent in this type of material. Glass ionomer cements also display a susceptibility to excessive hydration during the early stages of their setting reaction which results in an inferior cement. In addition, the hardened cement has a propensity to dehydration, brittle fracture, and erosion under acidic conditions.

Objective

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

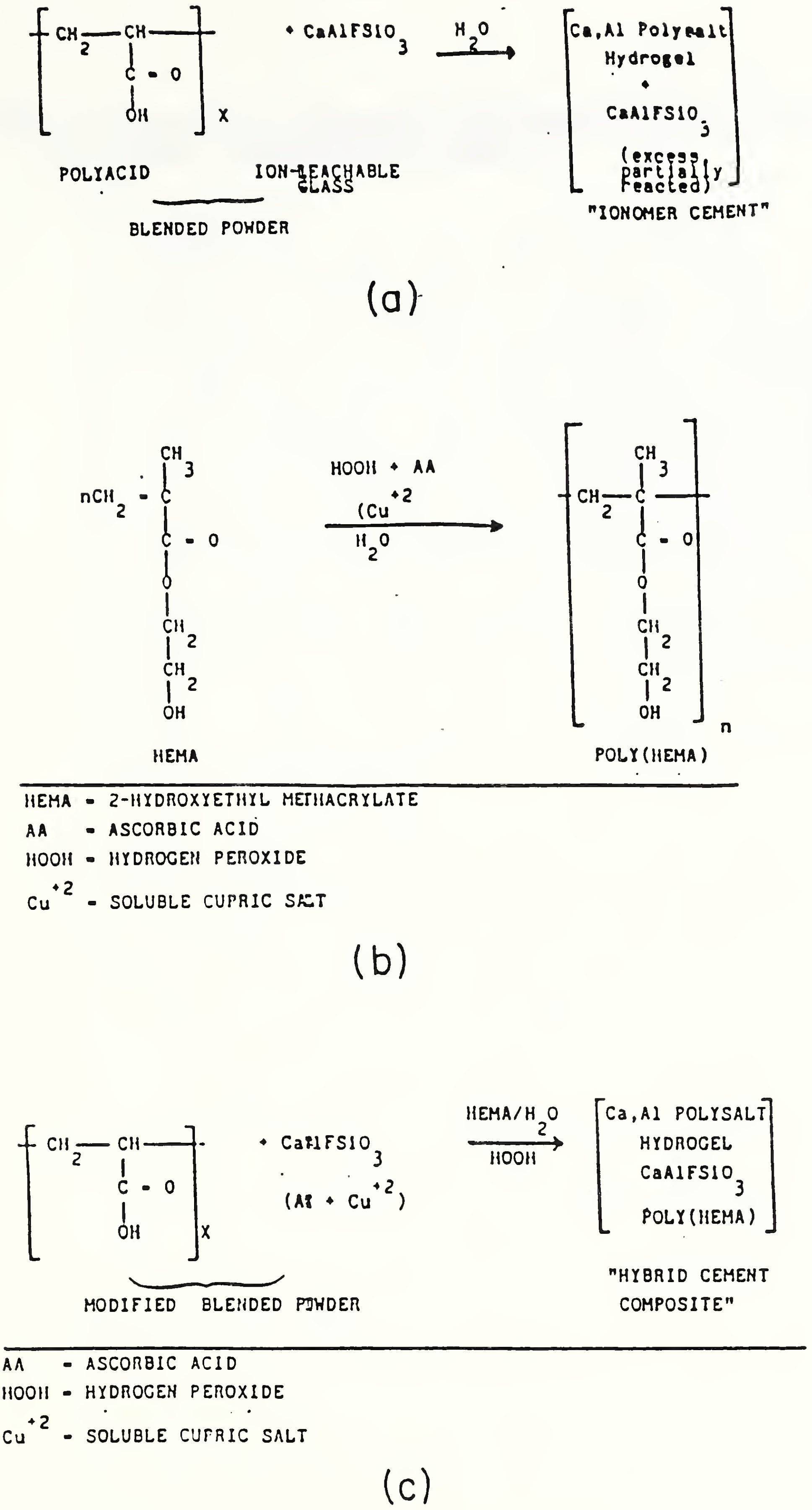
Phase I Formulation and Evaluation of New Cements

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

Our previous investigations demonstrated the feasibility of developing hybrid dental cement-composites (HCC's) from polyelectrolyte based cements (e.g. glass ionomer cements) and water soluble or compatible vinyl monomer and initiator systems (Fig. 3) These resin-modified glass ionomer cements exhibited a significant improvement in their resistance to brittle failure and usually displayed higher diametral tensile strengths than conventional glass ionomer cements. In this study we explored the feasibility of preparing polymer-modified glass ionomer cements from a water hardenable glass ionomer cement using aqueous solutions of various polymers (e.g. polyethylene oxide, polyvinyl alcohol, gelatin, etc.). This type of modified glass ionomer cement does not require the use of compatible resin and initiator systems, although these may be used along with the water soluble or compatible polymers. The use of the aqueous polymer solutions facilitated the mixing of the blended powder component (polyacid and ion-leachable glass) of the glass ionomer cement with water and yielded toughened cements with excellent diametral tensile strengths (Table 4). An abstract based on this work has been submitted for the 1989 AADR meeting.

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

Due to the higher priority assigned to part (a) of Phase I no additional work was performed on this project during this period.



HEMA - 2-HYDROXYETHYL METHACRYLATE
AA - ASCORBIC ACID
HOOH - HYDROGEN PEROXIDE
Cu^{+2} - SOLUBLE CUPRIC SALT

AA - ASCORBIC ACID
HOOH - HYDROGEN PEROXIDE
Cu^{+2} - SOLUBLE CUPRIC SALT

Fig. 3. Polymerization mechanisms for (a) conventional water hardenable glass ionomer cement, (b) aqueous free radical polymerization of water soluble monomer, and (c) hybrid cement composite (HCC).

TABLE 4

DIAMETRAL TENSILE STRENGTH (DTS) OF A POLYMER MODIFIED GLASS-IONOMER CEMENT (CHEMFIL II)

POLYMER	% b.w. in H_2O	POWDER* Liquid	DTS(S.D.) in MPa
PEO-8,000	6.4	8	27.8(3.6)
PEO-8,000	10.1	8	28.9(3.1)
PEO-100,000	1.0	8	31.0(4.7)
PEO-100,000	2.0	9	31.6(3.4)
PEG-20,000	2.3	7	32.1(3.4)
PEG-20,000	2.3	8	33.9(3.3)
PEG-20,000	9.9	7	26.2(1.9)
PEG-20,000	9.9	8	29.0(0.4)
GELATIN	5.0	7	19.7(2.3)
GELATIN	20.0	6.7	21.9(3.3)
			24.4(1.3)
			7d DTS

*CHEMFIL II POWDER

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

<u>Overview</u> (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

This study has as its goal the elucidation of the nature of the interfacial phase that forms between the filler and resin phases of dental composites. Previous studies of composites prepared using a conventional radiopaque glass filler (~45μm) demonstrated the significantly greater diametral tensile strengths (DTS) and transverse strengths (TS) of composites prepared with silanized (3-methacryloxypropyltrimethoxysilane, MAPS) versus those containing an equal amount of unsilanized filler (53). A similar study is in progress using a microfine glass filler (Degussa OX 50). Silanization required as expected a larger quantity of MAPS (~7% b.w. versus 0.5 b.w. for the conventional filler). For a visible light activated ethoxylated bisphenol A dimethacrylate resin (Esschem Co.) containing 50% b.w. of the silanized and unsilanized microfine glass filler, 24 hour DTS values of the respective silanized and unsilanized composites were 38 and 34 MPa, respectively. Apparently, at least as regards this mechanical property, there seems to be less of a reinforcing effect from silanized microfine glass compared to that of silanized siliceous macrofillers. The same ethoxylated bisphenol A dimethacrylate resin gave with 80-82% b.w. of the radiopaque macrofiller (silanized versus unsilanized) results similar to those we reported previously for the BIS-GMA/TEGDMA based composites; that is, the DTS value of the composites containing silanized macrofiller were almost twice that of similar composites formulated with unsilanized glass.

In a cooperative study with Drs. Katz and Singh of Rensselaer Polytechnic Institute, the elastic properties of composites prepared with a unsilanized and silanized radiopaque silica macrofiller (45μm) were evaluated using ultrasonic propagation techniques. Under dry storage conditions the composites had similar elastic properties [55].

In a related study using it was demonstrated the MAPS and related silane coupling agents were ineffective in conferring reinforcing properties (as measured by DTS) on various calcium phosphate fillers. Infrared analysis indicated that after washing with the solvent used in the silanization procedure, silane derived products were present on the calcium phosphate minerals. However, the interfacial bond appears to be weaker than that obtained with siliceous fillers. Preliminary results using a zirconate coupling agent, zirconium (IV) dimethacrylate, as a means of surface modifying calcium phosphate fillers appear to be more effective. [56,58].

In another study we have demonstrated the vulnerability of hydrophilic composites to the adverse effects of water. In Table 5 is shown the composition of an extremely hydrophilic resin system containing almost 50% HEMA (2-hydroxyethyl methacrylate) and chemically activated with N,N-dihydroxyethyl-p-toluidine (DHEPT). Composites prepared from this resin and a conventionally silanized radiopaque macrofiller (45μm) using a powder/liquid ratio of five exhibited excellent DTS (54 MPa) after one day storage in distilled water at 37°C. However, after two weeks of aqueous storage at 37°C, DTS had fallen to 44 MPa. This result probably reflects plasticization of the matrix by the sorption of water, which would in turn reduce the glass transition temperature of the composite. Degradation of the interfacial silane bond also may be affected, especially after more prolonged storage.

A water-saturated resin formulation based on that shown in Table 5 was prepared by the addition of 10.2% b.w. of distilled water. A single phase resin system resulted which when mixed with 5 parts b.w. of glass yielded a composite with a DTS of 46 MPa after one day storage in water at 37°C, similar to the value obtained from the "dry" hydrophilic composite after 14 days storage. Presumably, the lower DTS value is again mainly due to the plasticizing effect of water on the composite, although deterioration of the interfacial phase also may be occurring.

Phase II. Development of Improved Filler Systems for Composites and Cements.

Filler Systems Based on Silica

The effect of filler content on the characteristic strength (S_o) and Weibull modulus (m) has been evaluated for a BIS-GMA based composite using Diametral Tensile Strength (DTS) values. The resin consisted of 69.3% b.w. BIS-GMA and 29.7% b.w. TEGDMA activated with a visible light initiator system comprising 0.2% b.w. comphorquinone plus 0.8% b.w. ethyl 4-dimethylaminobenzoate. A commercial visible light source (Prismalite, L.D. Caulk Co.) was used to effect polymerization of the composite. The particulate macrofiller (45 μm) was a barium oxide containing silica silanized with 0.5% b.w. MAPS. On a weight/weight basis the filler/resin ratio (F/R) was varied from 1.5 to 5. For each F/R a total of 60 DTS composite specimens were prepared, stored in distilled water for two weeks at 37°C, and tested at a crosshead speed of 10 mm/min on a universal testing machine. Cylindrical specimens of approximately 6mm diameter x 3 mm height were used. Maximum likelihood estimates for m and S_o were determined by Newton-Raphson iteration as shown below:

Filler/Resin Ratio (wt/wt):	F/R	1.5	3	4	5
Weibull modulus	m	10.7	10.1	11.8	10.0
Characteristic Strength (MPa)	S_o	44.7	44.6	48.8	52.4

The Weibull modulus appears constant for all F/R at the 90% confidence level. The characteristics strengths for F/R ≥ 3 are statistically different at the 90% confidence level, using tables by Thoman, Bain and Antle. It appears that the Weibull modulus m of the resin governs the fracture strength distribution whereas the filler content affects the fracture strength (Fig. 4).

TABLE 5

EFFECT OF H_2O ON THE STRENGTH OF RESIN BASED COMPOSITES

FORMULATION AND EVALUATION OF A HIGHLY HYDROPHILIC RESIN BASED COMPOSITES

COMPOSITION OF RESIN

COMPONENT	WT%
BIS-GMA	37.35
TEGDMA	12.45
HEMA	49.80
DHEPT	0.40

COMPOSITION OF POWDER

SILANIZED BaO-SiO_2 COATED WITH 1% b.w. BPO

POWDER/LIQUID RATIO = 5

DIAMETRAL TENSILE STRENGTH (DTS) AFTER WATER IMMERSION AT 37°C

TIME OF IMMERSION IN H_2O	DTS (STD DEV) IN MPa
1 DAY	54.2 (4.2)
14 DAYS	43.8 (1.4)
1 DAY USING RESIN WITH 10.2% b.w. H_2O	45.6(2.0)

Filler Systems Based on Calcium Metaphosphates

This project represents a collaborative effort with B. Fowler of NIDR and S. Venz of Caulk/Dentsply.

Orthophosphate minerals such as tribasic calcium phosphate, various synthetic apatites and hydroxyapatite have been considered as fillers for resin based dental composites [56-58]. Because of their high refractive indices (e.g. 1.62 or greater) these types of orthophosphate minerals create a serious optical mismatch when they are used as fillers for current dental resin systems. Because of their opaque appearances, these composites lack the esthetics needed for the restoration of anterior dentition. Also, because of this optical mismatch between the resin and filler phases, these composites are ill-suited for photochemical polymerization. They can, however, be self-cured by the usual methods of ambient, chemical free radical polymerization (e.g. benzoyl peroxide and tertiary aryl amines).

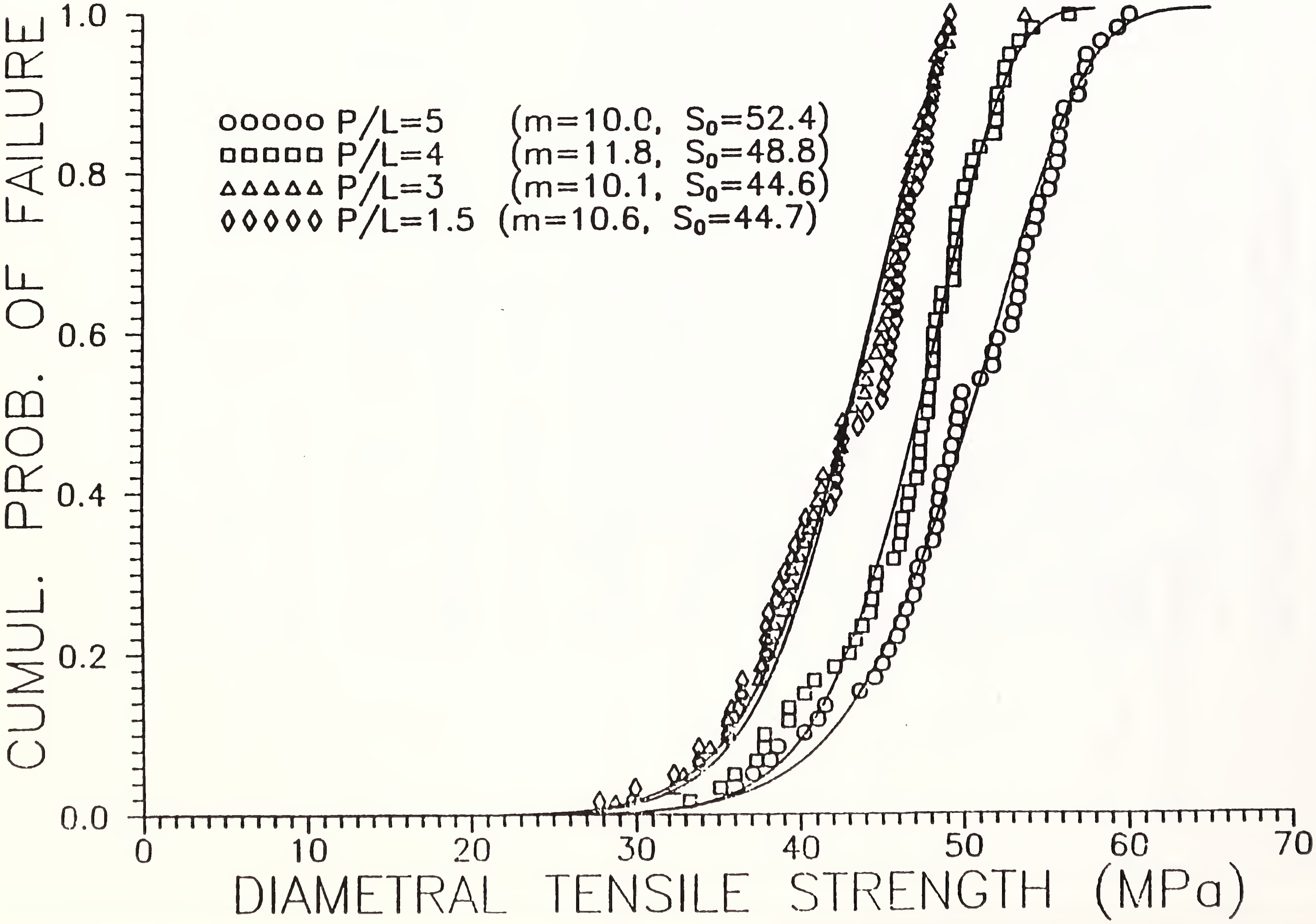
Calcium metaphosphates (CMP's) are a unique class of phosphate minerals having oligomeric or polymeric structures (Fig. 5), $[Ca(PO_3)_2]_n$, analogous to that of some calcium metasilicates, $[CaSiO_3]_n$. The PO_3 units are structurally linked to form chains that have lengths ranging from about 20 to 10,000 units (n = 10 to 5,000) [59] . Four different crystalline forms designated α, β, γ, δ and a noncrystalline or vitreous form of calcium metaphosphate are known. The approximate values of n are: 5,000 for the α and β forms; 200 to 600 for the γ and δ forms; and 20 for the vitreous form [59].

Physical and Chemical Properties of $Ca(PO_3)_2$

Thermal Stability and Melting Point. The thermal stabilities of these polymorphs increase in the δ-γ-β-α sequence [60-62]. The δ and γ forms convert into the β form at about 700°C and 500°C, respectively; the β form exists up to 963°C and then melts at 977°C. The α form exists between 963°C and its melting point of 984°C.

Indices of Refraction. Values for the crystalline α, β, γ and δ forms range from 1.57 to 1.59 and that of the vitreous form is 1.544 [61,63]. Thus unlike, many other calcium phosphate fillers, CMP's have refractive indices (~ 1.54-1.59) that are closer to those of many dental resin systems.

CUMULATIVE PROBABILITY OF FAILURE FOR 4 FILLER/RESIN RATIOS.



POLYMERIC STRUCTURE OF CALCIUM METAPHOSPHATES

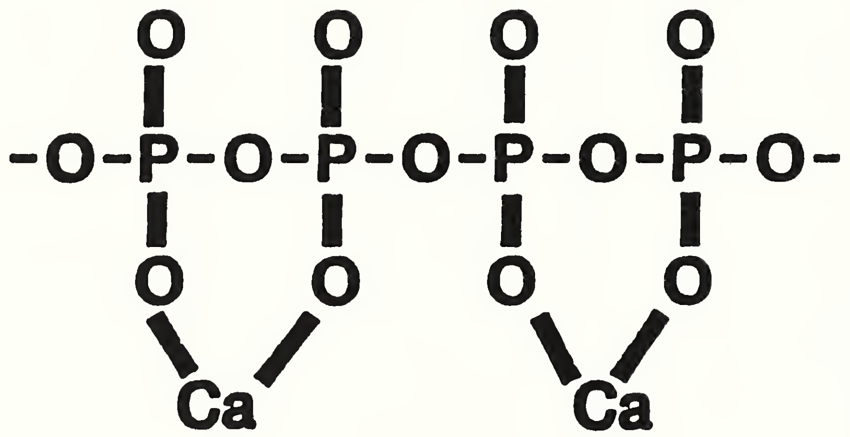


FIGURE 5.

pH of Water Slurry. A slurry of 0.2 mass % β-Ca $(PO_3)_2$ in water has a pH of 4.5 ± 0.1; vitreous-$Ca(PO_3)_2$ 0.5 to 5 mass % slurries have a pH of 3.5 ± 0.2.

Solubility in Water. The crystalline α, β, γ and δ forms are very insoluble in water at low pH; the vitreous form is more soluble than the crystalline forms [61,64]. Preliminary solubility values in grams per 100 ml of water at 22°C are: β-$Ca(PO_3)_2$, 0.01 g at pH 4.5 ± 0.1; vitreous - $Ca(PO_3)_2$, about 0.2 g at pH of 3.6 ± 0.1 on dissolution for three days. The corresponding solubilities of hydroxyapatite, the prototype of the mineral in tooth and bone, are 0.08 g at pH of 4.5 and, by extrapolation, about 1g at pH 3.6 [65].

Density. Calculated values in g per cm^3 for the α, β, γ, δ and vitreous forms of $Ca(PO_3)_2$ are: 2.96, 2.92, 2.85, 2.94, and 2.72, respectively [63]. The measured density of the β form is 2.82 [63].

Hardness. β-$Ca(PO_3)_2$ and vitreous-$Ca(PO_3)_2$ have Knoop hardness values in N per mm^2 of 191 ± 25 and 288 ± 2, respectively.

Preparation of Calcium Metaphosphates

The four crystalline and vitreous forms of $Ca(PO_3)_2$ can be prepared by appropriate heating of commercially available monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2.H_2O$, in the 150 to 1050°C range [60,61,64]. Procedures for preparation of the lower temperature forms, γ and δ of $Ca(PO_3)_2$, are reported in the literature [61,63].

β-$Ca(PO_3)_2$ Preparation. Heat $Ca(H_2PO_4)_2.H_2O$ at 150 to 180°C to remove hydrate water and form anhydrous $Ca(H_2PO_4)_2$; further heat to 250 to 300°C to effect condensation of $Ca(H_2PO_4)_2$ groups with release of two water molecules per formula unit to form $[Ca(PO_3)_2]_n$ chain structures. The $[Ca(PO_3)_2]_n$ (formula given without n hereafter) first formed on heating for a few hours at 250°C is noncrystalline. This can be converted to crystalline β-$Ca(PO_3)_2$ by the heating temperature and duration of heating in the 250 to 963°C range. The approximate temperatures and times, respectively, required for near 100% conversion to crystalline β-$Ca(PO_3)_2$ are: 250°C, 5 days; 500°C, 2 hours; 600°C, 1 hour; and 950°C, less than 10 minutes.

α-$Ca(PO_3)_2$ Preparation. The α-$Ca(PO_3)_2$ form exists between 963°C and its melting point of 984°C. Heat β-$Ca(PO_3)_2$ between 970 to 980°C for conversion to α-$Ca(PO_3)_2$ [60,66].

Vitreous-$Ca(PO_3)_2$ Preparation. Heat $Ca(H_2PO_4)_2.H_2O$ or $Ca(H_2PO_4)_2$ or any of the $Ca(PO_3)_2$ forms in a platinum crucible at 1050°C to form a $Ca(PO_3)_2$ melt; remove crucible containing melt at 1050°C and allow melt to rapidly cool in air at ambient temperature to room temperature [63,64,66].

Preparative Conditions that Influence and/or Control the Size, Shape, Texture, and Porosity of Calcium Metaphosphate Solid Particles. The dehydration of monocalcium phosphate monohydrate (Reaction I) and condensation of monocalcium phosphate (Reaction II) to form calcium metaphosphate result in the evolution of one and two molecules of H_2O, respectively; the overall reaction is given by Reaction III.

$$\text{I.}\quad Ca(H_2PO_4)_2.H_2O \xrightarrow{150^\circ C} Ca(H_2PO_4)_2 + H_2O$$

$$\text{II.}\quad Ca(H_2PO_4)_2 \xrightarrow{250^\circ C} Ca(PO_3)_2 + 2H_2O$$

$$\text{III.}\quad Ca(H_2PO_4)_2.H_2O \xrightarrow{250^\circ C} Ca(PO_3)_2 + 3H_2O$$

Rapid Dehydration and Condensation to Form β-$Ca(PO_3)_2$

If $Ca(H_2PO_4)_2.H_2O$ or $Ca(H_2PO_4)_2$ is heated directly at 500 to 950°C at atmospheric pressure the sudden evolution of water from the solid during the dehydration and/or condensation reactions results in very porous particles of β-$Ca(PO_3)_2$. For example, direct ignition of $Ca(H_2PO_4)_2.H_2O$ at 900 to 950°C for 3 to 20 minutes forms irregularly shaped crystalline birefringent particles of β-$Ca(PO_3)_2$ up to 200-300 um in size that have numerous craters on the surfaces and internal pores with diameters from about 1 to 5 um. The degree of porosity formed by heating directly at 900°C, e.g., 10 minutes, can be controlled and progressively reduced by further heating about 20°C below the melting point of 977°C for increasing time periods. The degree of formation of pores in $Ca(PO_3)_2$ particles prepared by the dehydration and condensation reactions (I and II) are affected by vapor pressure. Direct ignitions at 800°C for 15 minutes (from 25 to 800°C in about 5 minutes) under reduced pressure (26 Pa), atmospheric pressure (10^5 Pa), and under increasing water vapor pressure of about 5 to 30 X 10^5 Pa yielded porous to nonporous particles. Porous particles were obtained at 26 Pa, 10^5 Pa, and about 5 X 10^5 Pa of water vapor pressure; nonporous smooth surface particles were obtained between about 10 to 30 X 10^5 Pa of water vapor pressure. Mixtures of both porous vitreous-$Ca(PO_3)_2$ and β-$Ca(PO_3)_2$ can be prepared by heating $Ca(H_2PO_4)_2.H_2O$ or $Ca(H_2PO_4)_2$ at selected temperatures for specific times: direct heating at 500°C for 10 minutes mainly forms vitreous-$Ca(PO_3)_2$; after 30 minutes at 500°C, the product is about 25% vitreous and about 75% β-$Ca(PO_3)_2$; and after several hours at 500°C, it is essentially all β-$Ca(PO_3)_2$. The solid products formed by heating directly at 500°C are less porous than those heated directly at 900°C. In composites formulated from these fillers with cratered surfaces and pores, resin incorporation into these craters and pores is expected to physically increase adhesion between resin and filler and to increase the composite strength. (Preliminary tests showed composites formulated with 85 mass % porous β-$Ca(PO_3)_2$ and 15 mass % polyethylene have about 10 % higher diametral tensile strength than those from nonporous controls).

Progressive Dehydration and Condensation to Form β-$Ca(PO_3)_2$

If the dehydration and condensation reactions of $Ca(H_2PO_4)_2.H_2O$ are carried out progressively, e.g., (a) 150°C for several hours to effect dehydration, (b) 250°C for several hours to effect condensation, and (c) then heated at higher temperature to accelerate formation of β-$Ca(PO_3)_2$, 500°C for about 2 hours or 900°C for about 10 minutes, the particles are less porous have smoother surfaces than those formed by direct heating between 500 and 900°C.

Formation of α-, β- and δ-$Ca(PO_3)_2$ from the Melt

According to the P_2O_5-$2CaO.P_2O_5$ phase diagram [60], on cooling a melt of $Ca(PO_3)_2$ initially above 984°C, α-$Ca(PO_3)_2$ first crystallizes at 984°C and then converts to β-$Ca(PO_3)_2$ at 963°C which is the stable form on cooling to room temperature. On cooling melts of $Ca(PO_3)_2$, initially at 1050°C, at about 5°C per minute, the melts supercooled about 80°C below the crystallization temperature of α-$Ca(PO_3)_2$ and crystallization occurred rapidly between about 920 to 900°C. Under these cooling conditions along with quenching the sample to room temperature within about 10 to 30 minutes after crystallization occurred, the δ polymorph of $Ca(PO_3)_2$ predominately formed. If these first formed δ-$Ca(PO_3)_2$ crystals from the melt were heated at 900°C for several hours, they converted to the stable polymorph expected for this temperature, β-

$Ca(PO_3)_2$. Formation of δ-$Ca(PO_3)_2$ from the melt has apparently not been reported. Previous methods for δ-$Ca(PO_3)_2$ preparation, from $Ca(H_2PO_4)_2$ at about 300 to 600°C were shown to be unreliable [61,62]. The ground particles of δ-$Ca(PO_3)_2$ were tabular-like in contrast to the fibrous-like particles of ground β-$Ca(PO_3)_2$. Supercooled melts at 900°C that were seeded with a few crystals of β-$Ca(PO_3)_2$ rapidly solidified and formed β-$Ca(PO_3)_2$ crystals that were elongated and cleaved on grinding into fibers. Initial nucleation of the supercooled melts from point sources, a few β-$Ca(PO_3)_2$ seed crystals, resulted in radiating, directional, linear type growth. Rapid crystallization from the seeded supercooled melts promotes formation of longer β-$Ca(PO_3)_2$ crystals than those formed by diffusion in solid-state reactions. The α-$Ca(PO_3)_2$ form was not obtained from the melt under the above cooling conditions; seed crystals of α-$Ca(PO_3)_2$ to nucleate it in the melt were not available. Heating solid compositions of $Ca(PO_3)_2$ at 970 ± 2°C for sufficient time is reported [64,66] to form α-$Ca(PO_3)_2$. Since the α form exists in a narrow temperature range of 963 to 984°C, accurate and precise temperature control is necessary to prepare it.

Vitreous-$Ca(PO_3)_2$ Particle Sizes

The solidified vitreous-$Ca(PO_3)_2$ prepared by rapidly cooling the melt is a clear, transparent glass-like materials. The physical volume of the intact solid vitreous-$Ca(PO_3)_2$ is primarily limited only by the volume of the vessel used to prepare the melt. The particle sizes can be varied by conventional grinding techniques and sieving. A paper presented at the 1988 IADR meeting gave some preliminary results of using β-$Ca(PO_3)_2$ and vitreous $Ca(PO_3)_2$ in resin based composites [67]. A patent application also has been submitted.

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 agent (e.g. NPG, NTG) or comonomer such as NPG-GMA or NTG-GMA and PMDM, the diadduct of HEMA and pyromellitic anhydride [8,15,16]. The latter two bonding systems display significant adhesion to enamel as well as dentin.

PROGRESS REPORT

Phase I. Synthesis of Carboxylic Acid-Containing Monomers.

Further work was deferred on this project while waiting for a more complete characterization of the diadduct of t-butylaminoethyl methacrylate (tBAEM) with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, BTDA, by HPLC and NMR analyses.

Phase II. Aldehyde Based Bonding Agents

In its present version, the Gluma system (HEMA plus glutaraldehyde) for bonding composites to dentin involves the prior use of a bonding agent. In a cooperative study with E. Asmussen and R. Bowen a study was undertaken to determine if pretreatment of the dentin with solutions of amino acids and the incorporation of camphorquinone and selected monomers into Gluma would negate the need for a bonding agent. Using a solution of pyruvic acid and glycine for dentinal pretreatment, and an optimized adhesive mixture of glutaraldehyde, HEMA, BIS-GMA, camphorquinone and water, tensile bond strengths to dentin of 14.5 MPa and to enamel of 23.3 MPa were obtained. A bond strength to dentin of 13.4 MPa was obtained in a control experiment (Gluma & Bonding agent). This new type of Gluma bonding system thus gave acceptable bond strengths without the prior application of enamel bonding agents. A manuscript based on this work has been approved by WERB and submitted for publication.

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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, and, in some cases, to assess the extent of wear on the opposing enamel when the restorations are placed in stress-bearing occlusion (Class I and II). 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. (not active this period).

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).

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

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

Phase II. Wear of Hydroxyapatic Against Dental-Alloy Counterfaces. (new task).

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

D. 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($2.6\text{x}10^4$ $J^{1/2}$ $m^{-3/2}$). 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 for which more flexibility is expected, 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 [6].

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) 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.

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

Since glass-ionomer cements show good bonding properties to dental tissue [11], it was decided to include the evaluation of their wear behavior in our studies. The cure process of the glass-ionomer cements does not seem to be as viscosity limited as with the resin-based composites. Accordingly, higher degrees of cure can be reached at the in situ temperature with the former.

With the three commercial glass-ionomer materials studied, the wear resistance of the water-preconditioned specimens was good except that the incidence of catastrophic failure from brittle fracture during wear was frequent [12]. Specimens preconditioned in dilute lactic acid revealed considerable chemical dissolution as apparent from electron micrographs and accelerated wear. More recent work [13] on a commercial silver-sintered glass-ionomer cement showed that, although the wear resistance improved considerably, the susceptibility to brittle fracture and chemical dissolution in lactic acid were still serious problems. These problems stressed the need for appropriate 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 (For further details, 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].
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.

PROGRESS REPORT

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

No experimental activity in Phase I was undertaken during this reporting period. Our past work on commercial composites provided a sufficient basis to initiate research on 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

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

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

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

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

The 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 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.

Ten treatments were done 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.

With the radiopaque composite (Fulfil), which employs a hybrid, barium-modified glass filler, the greatest weight loss was observed using both APF treatments. Significant, but smaller, losses were observed using SnF_2 and NaF. SEM observations on the APF treated specimens revealed a porous structure which is attributed to the leaching out of the filler. SEM observations on the worn surfaces showed a smoothing out which resulted in a polymer-rich layer. This layer apparently reduced the extent of abrasion, thus the wear rates, in some cases, in the early regions of wear.

More recently, studies have been made on the visible-light-activated microfilled composite (Silux) which contains a quartz filler. In this case SnF_2 treatments produced the largest weight loss. With the other measurements the data are not sufficient as yet to make any judgement. Microdefect analyses employing a silver staining technique [17] have been started on both composites.

The early phases of this work were presented at the IADR Conference in March 1988 [18]. An abstract covering the later results will be submitted for the 1989 IADR Conference.

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

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

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

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

Background

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

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

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

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

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

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

An abstract covering these preliminary results has been submitted for the 1989 IADR Conference.

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

Background

The glass-transition temperature, T_g, in particular as a function of cure temperature, is an important parameter to facilitate the evaluation of the performance of resin-based composites. With free-radical activated systems, the degree of cure is limited by a critical viscosity at which the molecular motion effectively ceases, thus prohibiting further proximation of reactive species, which essentially terminates the curing process [22]. Since T_g is a manifestation of an isoviscous state, the viscosity depends upon T_g, which, in turn, depends upon the cure temperature. If the cure temperature is increased sufficiently, complete conversion may be obtained (at least in principle) for which the corresponding T_g is designated $T_{g\infty}$. For the flexible polymers, the value of $T_{g\infty}$ is low in comparison to that for a rigid polymer. Thus for the 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 [23] for pure BIS-GMA and 70/30 BIS-GMA/TEGDMA, both of which, especially the former, are rigid-polymer systems and, thus, have large values of $T_{g\infty}$.

D. Wear Instrumentation (New Task)

Background

The *in vitro* wear measurements mentioned throughout this chapter were made using a pin on disc apparatus described in Reference [24]. The original version was designed and assembled at the University of Indiana [25]. A second version was constructed at the National Bureau of Standards and essentially completed in 1976. This version was automatic, being programmed on a tape, but did not involve a central processing unit (CPU). The mechanical portion of the apparatus (involving unique components manufactured at NBS) was reinterfaced, and a programmable instrumentation controller with a CPU was incorporated [24]. This modification resulted in a more convenient, flexible, and reliable system, which has been used up to the present time. A large portion of our activity during this reporting period was dedicated to the design, acquisition, and construction of components to obtain the present version of a pin and disc wear apparatus for which the salient features are described below.

Phase I. Methodology for Improved Wear Apparatus

As a consequence of increased demand and new methodology in dental wear measurements, a new pin on disc wear apparatus has been designed and is being assembled. The new version has independent stepping motors as drives for the three rotating specimen discs and other mechanical controls. These motors are fully programmable with respect to angle, rate, and function, e.g., constant speed, sine function, ramps, or steps. They also eliminate the need for the positioning scanners used in the present version.

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

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

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

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

Most of the commercially available electronic components for the new wear apparatus have been acquired and tested during the last reporting period. These include the computer (programmable in BASIC), hard and soft disc drives, a printer, and a data acquisition control unit, which comprises an integrating voltmeter, a 20-channel relay multiplexer with thermocouple compensation, a 16-channel general purpose switch, an 8-channel power controller, a 3-channel counter, and a stepping motor controller. The stepping motors, their power supply and control circuits, encoders, and LVDT's and their conditioning circuits, pulse-interrupt circuit, and GPIB cables have been acquired, or designed and constructed, during this period. The stepping motor drivers are presently under construction.

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

The mainframe, which is the mechanical portion of the apparatus including the drive motors and rotating disc assembly, the pin assembly, wear measurements assembly, and cam lifting assembles for the pin and measurement devices is about 80% complete at the time of this writing. The remaining work on the entire apparatus will involve completion of the mainframe, electrical interconnection of the components, and computer programming, which are intended to be finished during the next reporting period.

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III Dental Alloys, Ceramics and Metrology

Overview

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

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

PROGRESS REPORT

Overview

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

Accomplishments

The objective of this part of the investigation was originally to explore the potential of using the gap of a porcelain veneered split metal ring as a means for determining the thermal stress compatibility between porcelain and metal [1,2]. As this project has progressed that objective remains in view; however, the plan has been expanded to explore the use of reliability analysis for prediction of fast-fracture compatibility. This will utilize finite element modeling (FEM), 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 phase is completed. (see NBSIR 88-3782)

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

This phase is completed (see NBSIR 88-3782)

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

This phase is in progress. A manuscript has been prepared for publication.

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

This phase will follow Phases I-III.

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

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

This is a new phase. The 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.

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

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

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

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

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

This phase 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 affect the PFM strength, but more data are needed.

There may be a difference between results with rounded corners and right angle sharp corners; the results are inconclusive at this stage due to very limited data.

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

PROGRESS REPORT

Overview

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

Numerous methods have been proposed in the past for determining various aspects of the casting of dental alloys. These have been discussed in NBSIR 86-3320.

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

Accomplishments

This study has now been completed. A manuscript entitled "Mesh Monitor Casting of Ni-Cr Alloys; Element Effects" has been accepted for publication in the Journal of Dental Materials:

In summary, the results of this investigation have shown that:

1) Mesh monitors are viable for assessing the effects of casting variables on the production of complete castings.

2) The casting of Ni-Cr alloys can be described by a casting equation [5]:

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

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

and

$$C_{v,t} = \ell n \left[\frac{2/3 + (C_v)^{1/2}}{2/3 + (1-C_v)^{1/2}}\right]$$

where C_v is the castability value, defined as the fraction of completely cast grid segments.

3) Changes in investment batch affect only the term "a" in eqn 1, changes in investment brand can affect both "a" and "b".

4) By solution of simultaneous equations, the effects of individual elements on a castability value can be determined. (see NBSIR 87-3539, 1987)

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

Accomplishments

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

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

E. Solderability

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

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

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

G. Metrology and Analysis: Occlusal Force Indicator.

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

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

H. Metrology and Clinical Performance

Phase 1. Development of Algorithms and Software for the Reduction of Data, Using the Weibull Distribution.

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

The Weibull distribution can be used to predict the characteristic lifetime of a given population even if only a few early failures have occurred. The process assumes a constant hazard rate and termination or censoring of the experiment at or near the last reported failure. This method has been applied to the bonding of fixed prostheses. The results have been submitted for publication. The shortcoming of this method is that all prostheses must be placed in service at the same time.

A computer program was written for the determination of the maximum likelihood estimators for the shape and scale parameters in time-to-failure experiments with various runout times (i.e. having a variable service time without failure at the time of the experiment termination). The calibration and verification of this program is as yet to be performed.

Phase II Analysis of Resin-Metal Bond Tests

This phase was reported on in NBSIR 88-3782.

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

In light of the previous findings [6] and the hypothesis put forth that the weighting factor for a mixed Weibull distribution, alpha, could be immersion-time dependent, an experiment was undertaken to determine the effect of immersion time on the Weibull parameters for a commercial dental composite. The material for which previous data were obtained is no longer available.

A different visible-light-initiated composite was used to determine if again a mixed Weibull distribution was observed after the composite had been exposed to a chemically active environment. In this study only ethanol was used as the food simulating liquid; however, the immersion time was taken to be the independent variable. The specific times of exposure were: 3 days, 3 weeks, 3 months and 6 months in 70% ethanol at 37 °C.

The diametral tensile strength was determined at a head speed of 10 mm/min. The preliminary results are shown in fig 1. The strength S_0 as determined by a Newton-Raphson iteration of the maximum likelihood equation is found in the table below.

TIME	m	S_0 (MPa)
1 day	16.3	45.1
3 days	17.2	46.4
3 wks	14.1	50.6
3 mos	10.8	38.6
6 mos	6.4	32.7

The preliminary evaluation shows that no obvious evidence exists for a mixed Weibull distribution for this composite even though the m value changes from an initial value of 17.2 to a final value of 6.4, which are statistically significantly different at a confidence interval of 90%, using the tables by Thoman, Bain and Antle [7].

It should be noted that the composite under evaluation differs from that used previously in that the previous composite was expected to be more hydrophilic than the current one (based on manufacturer's information).

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

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

The results from the study are expected to guide:

a) development of new cavity preparations.

b) clinical studies.

c) development of new materials.

d) development of restorative placement techniques.

J. Metrology: Sterilization of Dental Instruments

PROGRESS REPORT

Accomplishments

Phase I. Development of Plasmas.

It was found that even with a new vacuum chamber that the heating of the chamber walls was a problem. Experiments using prolonged exposure to microwave radiation with and without the concomitant vacuum showed that the heating is not due to the absorbtion of the electromagnetic radiation by the chamber, but only occurs when an active plasma is present. A glass desiccator proved to be an adequate vacuum chamber that permits exposures of longer than 2 minutes before reaching unacceptable temperature levels.

Phase II. Effects of Plasma on Spores.

The effect of the plasma on spores of Bacillus subtilis was determined by submerging dental burs in a spore solution and then exposing the burs to the plasma. The optimum pressure for the plasma was between 50 and 200 milliTorr, and the exposure time at which consistent inactivation of the spores occurred is 30 seconds. The spores were declared inactive if incubation of the dental bur in a tripticase broth at 37 °C for 7 days showed no macroscopic cultures. Positive controls verified the viability of the spores used in each experiment. Preliminary results have been accepted for publication.

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Conference/Special Meetings

Tesk, J.A., Chairman, Conference on Modern Instrumentation and Analysis Techniques. Planned for October 6-8, 1988.

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Invited Talks

de Rijk, W.G. The caries process and related measurements. Johns Hopkins U., March 28, 1988.

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DTS VALUE SHIFT AS A FUNCTION OF SUBMERSION TIME IN 70 % EtOH
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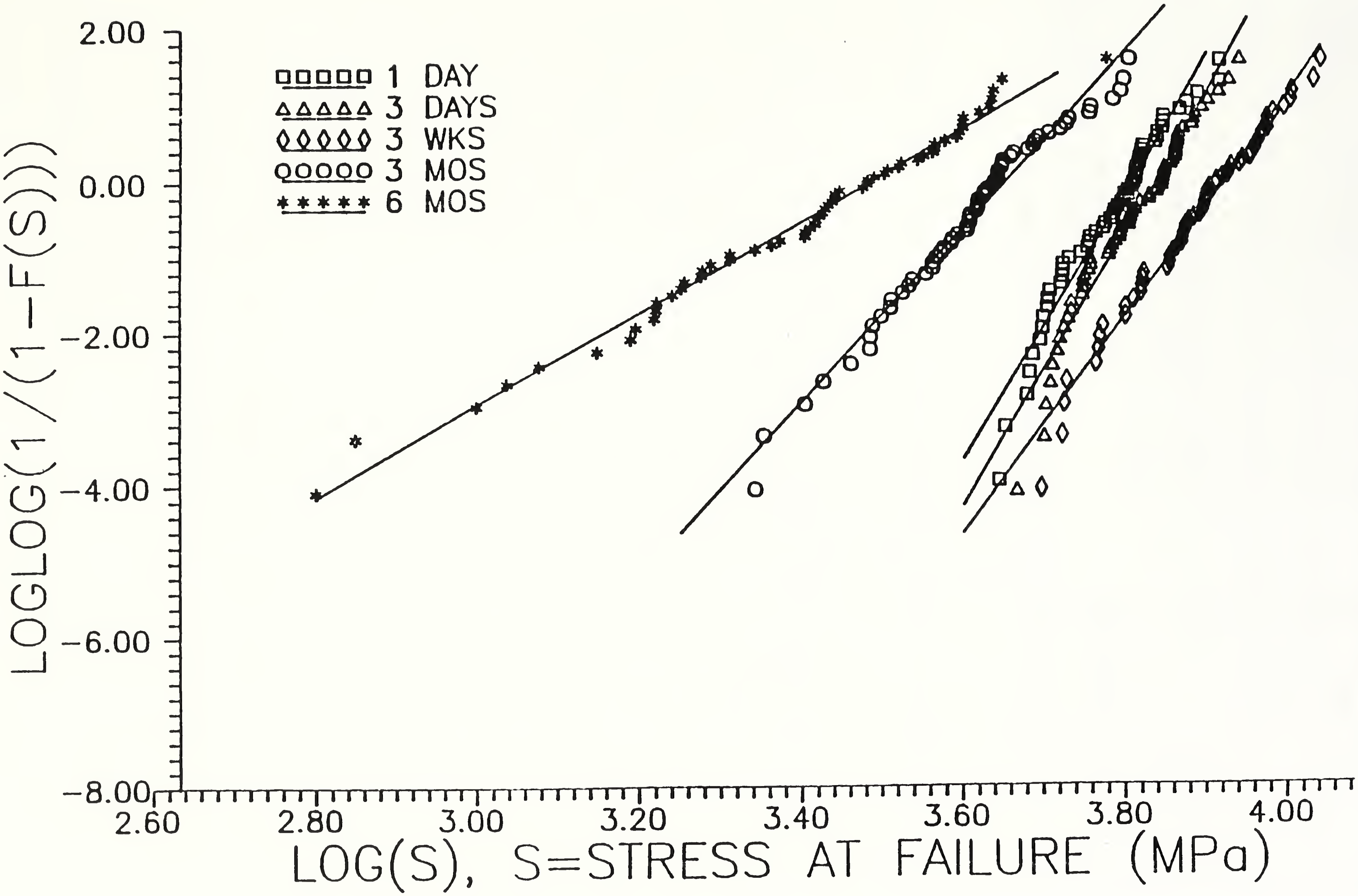

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant*

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

Dental engineering; dental restoratives; dental materials

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