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Properties and Interactions of Oral Structures and Restorative Materials

J. Tesk, J. Antonucci, G. Brauer, J. McKinney, R. Penn, J. Stansbury, W. de Rijk,
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U.S. DEPARTMENT OF COMMERCE
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Gaithersburg, MD 20899

Annual Report for Period
October 1, 1984 to September 30, 1985

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NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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

ABSTRACT

The research program described herein is designed to achieve a number of objectives leading to improved dental restorative materials, techniques and applications of dental materials science for improved dental health care in general. Some of the research in dental composites is directed toward developing generic systems potentially applicable to other composite applications, e.g., durable resin matrices, stronger more durable coupling between fillers and resins and improved reinforcement by defining the types, compositions 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 by wear and hardness measurement techniques, 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 of clinical results on wear and failure of composites with laboratory test data via a time to failure analysis. Metrology and analysis constitutes the underlying theme of investigation into porcelain-metal system, casting of dental alloys and expansion of 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 85 SIGNIFICANT ACCOMPLISHMENTS

- Tough, deformable dental-cement formulations which expand slightly on setting have been developed.
- Prepolymer resins for dental composites which reduce polymerization shrinkage and show promise for higher in vivo durability were also developed.
- Monomers which expand during free-radical polymerization were synthesized.
- Monomers with the potential to render dental resins radiopaque were also synthesized.
- A dental composite evaluated by diametral tensile testing was shown to undergo surface induced failure rather than internal-flaw induced fracture.
- Dental composite restoratives were found more prone to color changes on aging than denture base polymers or resin based synthetic teeth.
- Several cements that exhibit significant adhesion to stainless steel, porcelain and composites were developed.
- Composite formulations with improved resistance to oral food simulating liquids were developed and found to have acceptable properties.
- Glass ionomer cements were found to undergo catastrophic failure under all conditions of wear evaluation...preconditioning in air or lactic acid produced the worst results.
- An experimental composite formulation was found to have its wear unaffected by preconditioning in oral food-simulating liquids.
- The effects of investment variables (batch, brand) on a castability value for dental casting alloy were demonstrated.
- A mercury dilatometer was developed for measuring polymerization shrinkage or expansion of dental resins, composites and cements.
- The internal setting expansion of phosphate bonded dental investments was confirmed at low values, ~ 0.1 %, by refined experiments using strain gauges.
- The diametral tensile test was shown to be a viable method for evaluating tensile strength of dental composites and cements.

DENTAL AND MEDICAL MATERIALS GROUP

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PROPERTIES AND INTERACTIONS OF ORAL STRUCTURES AND RESTORATIVE MATERIALS

INTRODUCTION

The following pages contain reports on work involved with the development of basic generic science and engineering which is expected to be useful in the development or control of dental materials used for restorative or treatment purposes. Some of the developments involve investigations into new dental resin formulations (Part I) which might improve the performance of dental composites. Cements and adhesion to filler particles or tooth structure are also addressed in this part.

Part II deals with examination of the basic parameters affecting the wear and durability of materials with particular emphasis on dental composites. The resultant information is used to help guide developments in Part I.

Part III is concerned with dental casting alloys, and the strength of veneered dental systems, in particular, porcelain fused-to-metal. Factors affecting the castability of alloys and how to measure and define aspects of castability are addressed. Mathematical methods are employed to reveal effects of individual elements as well as other parameters. The strength of veneered systems is the characteristic receiving the most attention for the porcelain-fused-to-metal studies. Special emphasis is being placed on measurement techniques and flaw analysis.

I. COMPOSITES, CEMENTS AND ADHESION

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

PROGRESS REPORT

Overview

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

Cements in current use are far from ideal. Their relatively low mechanical properties, high solubility and lack of resistance to wear and disintegration deters their more extensive use especially for cementation of permanent protheses or 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] 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) non-inhibition of free radical polymerization; thus can be used in conjunction with composite filling materials, (4) compatibility with acrylic monomers which permits the formulation of hybrid composite-cements and (5) strong adhesion, even on prolonged water exposure, to non-precious metals, porcelain and composites.

Objective

The objective of this study was to evaluate these cements for various dental applications and to further improve desirable properties. To achieve this objective the following tasks were undertaken: (1) synthesis and evaluation of divanillates and polymerizable vanillates such as methacryloxyethyl vanillate and addition to these compounds of hexyl vanillate-ethoxybenzoic acid (HV-EBA) cements to improve mechanical properties; (2) quantitative measurements of the adhesive properties of HV-EBA cements; (3) formulation of intermediate restorative materials (IRM) incorporating monomers and reinforcing fillers with cement ingredients and determination of their mechanical properties; (4) synthesis of cements containing the potentially caries-reducing syringic esters and evaluation of properties of the resulting cements; (5) modification of these cements by addition of small concentrations of additives such as acids, metals or fluorides to improve their properties (6) furnishing of assistance and guidance to conduct investigations of the biocompatibility and toxicity of the cement and its ingredients and collaboration in studies of pulp irritation and in clinical studies at various dental research centers.

Accomplishments

Phase I -

(1a) Synthesis of Divanillates and Polymerizable Vanillates as Ingredients of Dental Cements.

To achieve higher strength and lower solubility, a series of esters of vanillic acid as well as compounds with multifunctional groups such as decamethylene or hexamethylene divanillate or methacryloxyethyl vanillate that react with metal oxides to give chain-extended products have been synthesized in the previous year. These compounds were incorporated successfully into dental cements and resulted in materials with improved properties. A manuscript describing these investigations in detail has been published in the Journal of Dental Research and in the Journal of Biomedical Materials Research. [2]

(1b) Adhesion of Cements to Various Substrates.

It was demonstrated previously that these cements have significantly stronger adhesion than ZOE to all substrates including dentin and enamel. Recent results show that the hexyl vanillate-EBA cements adhere especially well to non-precious metals, porcelain and composites. The joined specimens break cohesively close to or above the tensile strength of the cement. With acid-modified cements bond strengths as high as 19.9 MPa (2880 psi) have been obtained. Strength of the porcelain-to-porcelain, porcelain-to-stainless steel and porcelain-to-composite bonds after 24 hour storage in 37 °C water were 13.9 MPa (2020 psi), 6.9 MPa (1000 psi) and 4.9 MPa (712 psi) respectively.

(1c) Formulation of Intermediate Restorative Materials.

n-Hexyl vanillate-EBA-ZnO cements are compatible with acrylic monomers (dicyclopentenyloxyethyl methacrylate, cyclohexyl methacrylate). Such solutions mixed with powder, made up from silanized glass reinforcing agent and zinc oxide and containing suitable peroxide-amine initiator-accelerator systems, have good working properties and harden in a few minutes. The cured materials have both compressive and tensile strengths one and a half to three times that of eugenol-based intermediate restoratives. These cement-composites adhere strongly to composites, non-precious metals or porcelain (maximum bond strength 15.6 MPa). Rupture of the bond occurs as the result of cohesive failure. Because of their high strength and excellent adhesion, the cements, subject to their biocompatibility with dental tissues, show great promise as intermediate restorative resins and in the repair of fractured porcelain or porcelain to metal crown or bridges. Details of this investigation have been published. [3]

Phase II -

(1d) Synthesis and Evaluation of Cements with Syringic Acid Ester Ingredients.

Evaluation of mixes containing these potentially caries-reducing esters, n-hexyl vanillate, EBA and zinc oxide powder are rapid setting, water insoluble, possess high strength. [4,5] The syringate cements, compared with the commonly used ZOE materials, have improved compressive and tensile strength, lower water solubility, do not inhibit polymerization, and are compatible with acrylic monomers. They bond significantly to resins, composites, and non-precious metals.

The cements, because of the syringate ingredient, may possess caries-reducing properties. Thus, perhaps in conjunction with fluoride additives, they would be useful as luting agents, insulating bases, pulp capping agents, root canal sealers, soft tissue packs, or intermediate restoratives.

(1e) Modification of Cements by Incorporation of Additives.

Addition of small concentrations of acid, metals or fluorides to vanillate or syringate dental cements was studied to improve their physical properties and anticariogenic behavior. [6] Incorporation of acids into cement formulations lowers their setting time. Coating a portion of the zinc oxide powder ingredient with propionic acid offers a convenient way of adjusting the curing rate most suitable for clinical applications. The resulting cements are nonbrittle, have high strength, low solubility and bond strongly to non-precious metals, porcelain or composites. Cements with zinc undecylate are flexible and may be useful as soft tissue packs. Metallic powders do not act as reinforcing agents for these cements.

Hexyl vanillate or ethylhexyl syringate cements can be prepared by adding 0.1 percent to 1 percent fluoride salts such as NaF, ZrF_4, ZnF_2 or dimethylaminoethyl methacrylate hydrofluoride to the powder ingredient. Rate of fluoride released is dependent on the solubility of the fluoride in water and decreases rapidly within the first few days after exposure to the liquid.

Phase III - Study of Biocompatibility, Toxicity and Clinical Usefulness

(3a) Synthesis of Materials for Pre-clinical and Clinical Studies.

Vanillate and syringate esters synthesized in this laboratory have been made available to many researchers on request. Hexyl vanillate is now commercially available from two manufacturers of specialty chemicals.

(3b) Toxicity and Biological Evaluation of HV-EBA-ZnO Cements.

The biological safety evaluation of the hexyl vanillate (HV)-EBA-ZnO cements has been completed. [7] Most ingredients of the cement gave a negative hemolysis test. o-Ethoxybenzoic acid, however, gave a positive result for rabbit red blood cell hemolysis. Oral LD_{50} in mice varied from 0.70 g/kg for o-ethoxybenzoic acid to over 1.00g/kg for n-hexyl vanillate and $ZnO-Al_2O_3$-hydrogenated rosin powder. The cloning efficiency test for EBA and the cement powder were negative at all concentrations whereas concentration above 25µg/ml HV resulted in a positive test. Ames mutagenicity tests for EBA, HV, $ZnO-Al_2O_3$ hydrogenated rosin powder and cement extract using salmonella strains TA 97, TA 98, TA 100 and TA 102 were negative. Thus, these results and those obtained previously [8] indicate that none of the ingredients of HV-EBA cements is toxic or mutagenic.

(3c) Biocompatibility of Syringate-Vanillate-EBA-ZnO Cements.

Studies by Dr. C. Siew of the American Dental Association Health Foundation evaluating the biocompatibility of the ingredients of ethylhexyl syringate-HV-EBA-ZnO cements are nearing completion.

(3d) Application for Periodontal Dressings

Studies by Rubinoff and Greener [9] using HV-EBA-ZnO formulations containing 12.6 percent Crisco as periodontal dressings showed that these compositions had physical properties equal to or superior to those of commercial dressings. Their ease of mixing and clean handling properties together with their non-eugenol composition indicate that these materials show promise as periodontal dressings.

(3e) Application as Endodontic Sealers

Endodontic sealers prepared from HV-EBA-ZnO and 10 percent $BaSO_4$ sealed significantly better at room temperature or 37 °C than eugenol containing controls. Implantation studies in rabbits showed that the biocompatibility of this sealer was equivalent to that of Grossman's cement.[10]

Conclusion

Based on the results of the biocompatibility tests it was concluded that clinical evaluation of the HV-EBA cement could proceed. The cement is now being made available to interested parties for clinical studies.

B. Changes in Esthetic Properties of Dental Resins on Aging.

PROGRESS REPORT

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 esthetically undesirable color changes. Many of these changes are the results of photochemical reactions of ingredients of the composite caused by exposure of the restoration to various energy sources. Since clinical studies to determine color stability of restoratives are time-consuming, accelerated aging tests have been suggested to correlate laboratory findings and clinical performance. Most of these tests are based on short-term (24 hour) exposure of the materials to light sources or heat often in an aqueous environment.

Objective

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

Accomplishments

We found that dental composites are more susceptable to undergo color changes on aging (especially on exposure to radiation) than denture base resins or plastic teeth. Therefore, a series of composites of the chemically cured (traditional, hybrid and micro-filled), light cured (traditional and micro-filled) and traditional (combined light and chemical cured) type were exposed to the Xenon and RS lamp for time periods ranging from six hours to seven days. [11] Irradiation of the materials by the RS lamp and in air produced more discoloration than exposure to the Xenon lamp in water. Visible light cured materials were more color stable than chemical cured ones. Light shades were more susceptible to color changes than dark shades of the same brand. Exposure of composites to 60 ^{o}C in the dark lead to much more rapid discoloration for materials stored in water than in air. Thus, most chemically activated composites when stored in water showed distinct color changes after one month whereas those stored in air had similar discoloration after exposure for three or more months. Clinical investigations to confirm what laboratory conditions for color stability tests best correlate with the color changes of restoratives in the mouth are available at present only for the chemically cured materials.

A liquid chromatograph has been set up to analyze the ingredients of the composites studied in the above investigation. Using a C-18 capped-silica column elution peaks for various peroxides, monomers, and amine accelerators have been established. Ingredients of one paste have been analyzed.

C. Study of Adhesion and Adhesion Promoting Agents to Dentin.

PROGRESS REPORT

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 micro-organisms and liquids by sealing the marginal areas of the restoration. With such a material, sealing of incipient carious lesions could be realized. An adhesive cement could lead to less invasive cavity preparations resulting in decreased loss of sound tooth substance.

Introduction

Many procedures to obtain permanent bonding to enamel or dentin have been suggested. Pretreatment of enamel, with dilute acid enhances adhesion of restorative resins to enamel, but is contraindicated for dentin. There are many constraints inherent in the long term bonding to dentin [12-15] 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 [16] and to dentin with tri-n-butylborane oxide as initiator. [17,18] 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. [19] A mixture of a phosphorus ester of BIS-GMA and diluent monomer polymerizable by peroxide, tertiary amine and sulfinic acid salt has been introduced commercially as a dentin-composite bonding agent. [20] Monomers with hydrophobic and hydrophilic moieties such as 4-methacryloxyethyl trimellitic anhydride (4-META) and the diadduct of hydroxyethyl methacrylate and pyromellitic anhydride (4-PMDM) bond dentin to acrylic resins. [21,22] Most effective are successive treatments of the dentin surface with ferric oxalate, a 5 to 10 percent acetone solution of a glycine derivative (adduct of N-phenyl or N-p-tolylglycine and glycidyl methacrylate) followed by a 5 percent solution of 4-PMDM in acetone. [22] Another good bonding agent to dentin is the mixture of 2-hydroxyethyl methacrylate and glutaraldehyde.[23-25]

Objective

The objective of this study has been to synthesize specific monomers or oligomers such as allyl 2-cyanoacrylate or oligomers of 2-isocyanatoethyl methacrylate and to prepare suitable formulations using these ingredients which may bond to dentin in an aqueous environment.

Accomplishments

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

A copolymer was synthesized by the reaction of n-butyl methacrylate (35 wt percent), ethyl acrylate (35 wt percent) and 2-isocyanatoethyl methacrylate (30 wt percent) in ethoxyethyl acetate with azoisobutyronitrile as initiator. The vitreous colorless solid containing pendant isocyanate groups as established from infra-red spectra will be reacted with mineralized tissue such as bone or dentin to determine if grafting of this polymer and collagen containing surfaces takes place.

To this prepolymer methacrylate side chains could be grafted through the isocyanate groups. The prepolymer dissolved in 2-ethoxyethyl acetate was reacted with 2-hydroxyethyl methacrylate in a nitrogen atmosphere and in the presence of dibutyl tin dilaurate. A hard solid slightly tan polymer was recovered. Infra red spectra indicated that this material contained urethane and methacrylate groups, but few unreacted isocyanate groups.

Phase II - If appropriate, proceed to arrange pre-clinical trials.

This study has not progressed to the state where preclinical trials are warranted.

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2. Modification of Cements Containing Vanillate or Syringate Esters, G.M. Brauer, J.W. Stansbury and D. Flowers. (Submitted for publication -Dent. Mat.)

Invited talks

"New Adhesive Dental Cements from Hexyl Vanillate-EBA-Zinc Oxide. Academy of Dental Materials, Feb. 1985.

Contributed talks

"Properties of Vanillate and Syringate Cements Containing Various Fluorides", J.W. Stansbury and G.M. Brauer. IADR/AADR meeting 1985.

"Color Changes of Composites on Exposure to Various Energy Sources", G.M. Brauer and J.W. Stansbury, IADR/AADR meeting 1985.

"Biological Safety Evaluation of a Newly Developed High Strength, Acrylic Resin Compatible Adhesive Cement", C. Siew, S. Gruninger, R. Hsu, G.M. Brauer, J.A. Tesk, IADR/AADR meeting 1985.

"Modification of Cements Containing Vanillate or Syringate Esters. D. Flowers and G.M. Brauer, Chemical Society of Washington, April 1985.

D. Monomers Which Polymerize with Expansion

Overview

A major deficiency inherent in all commercial monomers utilized in dental adhesives and composites is the shrinkage that accompanies their polymerization. The stresses resulting from this contraction of the resin often are manifested as microcracks, marginal gaps or by debonding at the filler particle interface in composites. Efforts to minimize the degree of polymerization shrinkage have included the use of hydrophilic monomers to promote a compensatory hygroscopic expansion by water sorption [1], reduction in the proportion of diluent monomer used [2] and the utilization of prepolymers. [3] In a different approach, which directly addresses the problem of polymerization shrinkage, our effort has been aimed at preparing novel spiro orthocarbonate monomers which will expand upon polymerization to counter the contraction of conventional monomers.

PROGRESS REPORT

Phase I - Synthesis

This investigation required the synthesis of new monomers capable of free-radical polymerization with an accompanying expansion in volume. Further, these monomers should contain substituents which provide for polymers with glass transition temperatures that are comparable to commercial materials. A previously reported method for preparing unsubstituted, symmetrical spiro orthocarbonates [4] was not applicable for the synthesis of substituted, asymmetric spiro monomers. Therefore, a new procedure was developed in which a high energy, cyclic thionocarbonate was utilized as an intermediate in the preparation of spiro orthocarbonates. This was accomplished by the reaction of a 1, 3-diol with thiophosgene in the presence of dimethylaminopyridine (DMAP) at 0 °C. (Figure 1) The synthesis of 5,5-dimethyl-1,3-dioxa-2-cyclohexanethione (1) was the first time that any

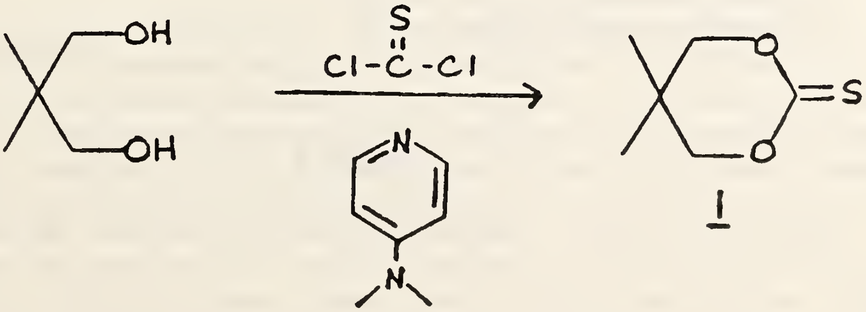
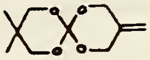
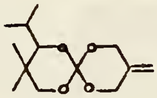
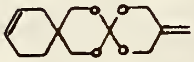


Figure 1

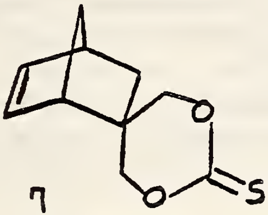
six-membered thionocarbonate had been isolated. This reactive intermediate yielded the new monomer, 3,3-dimethyl-9-methylene-1,5,7,11-tetraoxaspiro [5.5] undecane (2) at room temperature, whereas spiro orthocarbonates synthesized by prior techniques required prolonged heating at >100 °C. Other monomers (Table 1) with higher degrees of substitution were prepared by this same technique. It is apparent that the substituents must be chosen to maximize the asymmetry of the compound if highly substituted monomers with low melting points are to be obtained.

Compound	Spiro orthocarbonate monomer	mp (bp)
2		34°C (76°C/2mm)
3		(102°C/0.5mm)
4		28°C (80°C/3mm)
5		52°C (125°C/0.3mm)
6		(75°C/0.3mm)

no. 2: 3,3-dimethyl-9-methylene-1,5,7,11-tetraoxaspiro [5.5] undecane
no. 3: diethyl substituted
no. 4: dimethyl-isopropyl substituted
no. 5: cyclohexene substituted
no. 6: 3,3-dimethyl-9-methylene-1,5,7,12-tetraoxaspiro [5.6] dodecane

Table I

While thionocarbonates were originally obtained in yields of 50 percent or less, the synthetic procedure has been refined to achieve greatly improved yields. To demonstrate this more efficient technique, the yield of thionocarbonate 1 was increased from 50 to 96 percent and the highly substituted 7 was prepared in 82 percent yield compared to a 5 percent yield in the initial synthesis.



7

Figure 2.

A spiro monomer containing a seven-membered ring (6) has been synthesized. This liquid monomer is expected to ring open more readily due to additional strain and provide a greater degree of expansion than monomers based on six-membered rings.

The preparation of nitrogen substituted spiro orthocarbonates which should give rise to stiff urethane linkages in the ring opened polymers has been initiated. A cyclic thiourethane (8) obtained from *t*-butyl aminoethanol has been synthesized. An attempt to produce the nitrogen containing monomer (9) was unsuccessfully carried out. The steric hinderance of the *t*-butyl group on nitrogen is likely to blame for the failure to form the spiro linkage. The cyclic thioamide from methylaminoethanol will be prepared and subjected to this same reaction.

8 9

Figure 3

<u>Phase II and III</u> - Formulation and Evaluation

While these spiro monomers are sluggish to homopolymerize, they readily form copolymers with the more reactive, acrylate monomers used in dentistry. In initial formulation work it was found that TEGDMA could be replaced entirely with the liquid spiro monomer (3) which served as diluent monomer for the bis-GMA. Upon curing, this composite resin exhibited a DTS value which was only about 5 percent less than the control while the shrinkage evaluation showed a slight volume expansion occurring after the initial polymerization shrinkage.

References

[1] Derman, K., Rupp, N.W. and Brauer, G.M. Effect of Hyrophilic Diluents on the Properties of Cured Composites, J. Dent. Res. 61 1250-1254, 1982.

[2] Brauer, G.M., Dulik, D.M., Hughes, H.N., Derman, K. and Rupp, N.W. Marginal Adaptation of BIS-GMA-based Composites Containing Various Diluents. J. Dent. Res. 60 1966-1971, 1981.

[3] Antonucci, J.M. New Monomers for Use in Dentistry, Biomedical and Dental Applications of Polymers. Plenum Publishing Corp. 357-371, 1981.

[4] Bailey, W.J. and Endo, T. Synthesis of Monomers that Expand on Polymerization. J. Polym. Sci., Polym. Chem. Ed. 14 1735-1741, 1976.

Publications

1. Intermediate Restoratives from n-Hexyl Vanillate-EBA-ZnO-Glass Composities, G.M. Brauer and J.W. Stansbury, J. Dent. Res. 63, 1315-1320 (1984).

2. Divanillates and Polymerizable Vanillates as Ingredients of Dental Cements, J.W. Stansbury and G.M. Brauer, J. Biomed. Mat. Res. 19, 715-725, (1985).

Patents

1. Biocompatible Cemetitious Compositions, G.M. Brauer and J.W. Stansbury, U.S. Patent 4,486,179, Dec. 4, 1984.

Manuscripts under review

1. The Effect of Inhibitors, Accelerators, Cross-linking Agents and Monomers on the Properties of Bone Cement, G.M. Brauer, D.R. Steinberger, and J.W. Stansbury (submitted for publication to J. Biomed. Mat. Res.).

2. Modification of Cements Containing Vanillate or Syringate Esters, G.M. Brauer, J.W. Stansbury and D. Flowers. (Submitted for publication -Dent. Mat.)

Contributed talks

"Properties of Vanillate and Syringate Cements Containing Various Fluorides", J.W. Stansbury and G.M. Brauer. IADR/AADR meeting 1985.

"Color Changes of Composites on Exposure to Various Energy Sources", G.M. Brauer and J.W. Stansbury, IADR/AADR meeting 1985.

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

This part of the annual report is divided into four distinct sections:

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. Preclinical and Clinical Testing.

I. Improvement of Dental Resin Systems for Composites and Sealants.

Overview (composites)

The quest for a durable, esthetic, adhesive and biocompatible material suitable for the restoration of lost tooth structure has long challenged dental materials researchers. A significant step toward the realization of this goal was the development of resin based dental composites which overcame many of the shortcomings of the silicate cements (purely inorganic composites) and unfilled resin restoratives (purely organic composites based on methyl methacrylate and its polymer). The synthesis of BIS-GMA (an offspring of the marriage of epoxy and acrylate chemistry) by Bowen, ushered in the modern era of resin based dental composite restorative materials and also dental sealants [1,2]. The essential components of dental composites are: (1) a resin system comprising one or more vinyl monomers which on polymerization forms the matrix or continuous phase, (2) reinforcing fillers such as silanized glass, quartz, other ceramics, organic and hybrid organic-inorganic powders of various sizes and shapes 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 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).

Objective

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

Introduction

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 application [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 degradative reactions not only in the polymeric binder and critical interfacial phase but, in some cases, even in the filler phase as well [20-23]. Two related approaches have been initiated in our laboratories as methods to enhance the OER of these materials. One involves the use of hydrophobic resin systems that have solubility parameters lower than that prevalent in the oral environment [24,25]. The other is aimed at increasing the degree of polymerization and the crosslink density of resin systems by methods compatible with the clinical situation [26-29]. The first approach involves the synthesis and formulation of resins that yield polymers containing significant amounts of fluorocarbon or siloxane segments to confer on dental materials the necessary hydrophobicity and solubility parameters to resist the detrimental effects of the oral environment [24,25,30,31]. The second approach, which also may encompass the first approach, involves the synthesis and formulation of multifunctional methacrylates, multifunctional chain transfer agents and other types of network forming agents that can augment the degree of cure and crosslink density [27,28,32]. Emphasis also is directed to monomers that should have minimal polymerization shrinkage [32]. An ancillary part of this approach also involves the development of more efficient initiator systems for ambient polymerizations of dental resins in a more uniform fashion [27].

PROGRESS REPORT

Phase I - Synthesis, Formulation and Evaluation of Resin Systems.

(1) Synthesis and characterization of the monomers, PFUMA; BIS-GMA/2-1EM, BIS-GMA/MPDMS were achieved as outlined in Figures 1-3.

a. Synthesis of a Polyfluorinated Prepolymer Multi-functional Urethane Methacrylate (PFUMA).

Urethane methacrylate resins yield composites of high strength but with water sorption (WS) similar to BIS-GMA-composites. The rationale of this study was to prepare a more hydrophobic urethane methacrylate resin. The polyfluorinated oligomeric polyol (PFP) used in the synthesis of PFMA was converted to a multifunctional urethane methacrylate using the difunctional monomer isocyanatoethyl methacrylate (IEM) as outlined in Figure 1. IEM, via its NCO group, reacts with the pendant OH groups of PFP yielding the polyfluorinated prepolymer monomer, PFUMA, which contains pendant urethane-ethyl methacrylate groups. PFUMA is a pale yellow liquid of greater viscosity and cohesive energy density than the previously synthesized PFMA (Figure 4). PFUMA also has a higher refractive index than PFMA (1.4347 vs 1.4197) which may make it more optically compatible with radiopaque glass fillers than PFMA. Structural confirmation by elemental, infrared and NMR analyses has been obtained. As was the case wth PFMA, PFUMA is miscible with a variety of diluent monomers (Figure 5). A preliminary study of several PFUMA based composites indicate that they are somewhat stronger (e.g. DTS=47 MPa) than similar PFMA based composites and have WS values almost as low. They have polymerization shrinkages that are significantly lower than several commercial composites (see Table 1). Detailed results of this study were presented at the 1985 AADR/IADR Meeting and at the Second International Conference on Polymers in Medicine in Capri, Italy, June, 1985. A manuscript has been prepared for publication.

b. Dental Resins for Increased Degree of Polymerization and Crosslink Density.

Synthesis of a Diurethane tetramethacrylate (BIS-GMA/2-IEM). - The diadduct of BIS-GMA and IEM was prepared as shown which further shows the utility of IEM as a reagent for urethane methacrylate formation. (Fig. 2) BIS-GMA/2-IEM is an almost colorless liquid somewhat less viscous than BIS-GMA despite its greater bulk (molecular weight = 822). Composites based on this tetrafunctional, bulky monomer have acceptable mechanical strength (e.g. DTS = 47 MPa). Other properties (e.g. degree of cure, polymerization shrinkage compatibility with other base monomers, etc.) are under study.

Synthesis of a Disiloxane Tetramethacrylate. Again from BIS-GMA, a unique tetrafunctional vinyl monomer of greater flexibility was prepared using 3-methacryloxpropyldimethylchlorosilane (MPDMS) as shown in Fig. 3. BIS-GMA/MPDMS was isolated in excellent yield as a pale yellow liquid with a viscosity significantly less than that of BIS-GMA despite its much greater bulk (molecular weight = 880). Infrared analysis indicated that virtually all the OH absorption of BIS-GMA had disappeared. The resin polymerizes by the usual free radical methods. A preliminary investigation of a composite prepared with this unique monomer alone revealed that an extremely high powder/liquid ratio of 6 was achievable using a conventional silanized barium oxide glass. That is, the filler content of these composites was 86% by weight (~70% by volume); diametral tensile strength of visible light cured composites was 42 MPa. Other properties of this unique resin (especially its potential use as a low shrinking diluent monomer) and its composites are under investigation.

(2) Formulation of resins and composites based on the newly synthesized monomers and PFMA (Figure 4) with various diluent monomers including the disiloxane diluent monomer, BIS-MPTMS (Figure 5).

a. Using diluents such as BIS-MPTMS, several visible light activated PFMA based composites have been prepared having acceptable mechanical strength and both low water sorption and polymerization shrinkage.

b. Formulation and Evaluation of Composites Utilizing a Disiloxane Diluent Monomer (BIS-MPTMS).

This task was directed at assessing the effect of bis-(methacryloxypropyl)tetramethyldisiloxane, BIS-MPTMS, as a diluent monomer on the properties of dental composites based on BIS-GMA, BIS-IPMA, 2,2-[p-(methacryloxyisopropoxy)phenyl] propane, and other base monomers (Table 2). The details of this study were presented at the 1985 IADR/AADR meeting and a manuscript has been prepared for publication [25]. The salient point is the maintenance of the good mechanical properties of the base resins even though significant amounts of the very flexible disiloxane diluent are used (Table 3). Water uptake for these siloxane composites is generally less than for similar composites using TEGDMA as a diluent (Table 4). The use of the less viscous, highly flexible BIS-MPTMS in place of TEGDMA also permits higher filler loadings than feasible with BIS-GMA which also contributes to the lower water sorption values. This unique diluent monomer is also compatible with some hydrocarbon urethane methacrylate monomers, PFMA and PFUMA. Several of these siloxane-containing composites exhibited significantly improved OER's [25].

c. The Effect of Diluent Types and Concentrations on Polymerization Conversion and Shrinkage

The results of this study are summarized in Figure 6. For pure BIS-GMA resin, the polymerization shrinkage (PS) is low but the degree of conversion (DC) is also low (about 33 percent); i.e., as the diluent concentration increases both DC and PS increase. With the more bulky type of diluent monomers (e.g., BIS-MPTMS and EPBADMA, Figure 5) the increase in PS with diluent concentration is more moderate than that observed with increasing amounts of TEGDMA. Details of this study were presented at the 1985 AADR/IADR meeting.

Phase II - Prototype Composite for Clinical Evaluation

A chemically activated, powder/liquid, PFMA composite formulation using a conventional fused quartz filler has been delivered to Dr. Joseph Moffa of USAIDR for evaluation.

II. Improvement of Dental Cements

Overview

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

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

Objective

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

Introduction

A novel, versatile class of dental cements, non-aqueous polycarboxylate cements (termed halatopolymers), were developed from the commercially available C_{36} and C_{54} hydrocarbon polycarboxylic acids, designated dimer (DA) and trimer (TA) acids. The divalent metallic dimerates and trimerates matrices of these cements are halatopolymers, a term coined to denote their dual salt-like and polymer-like character. All of these cements have water repellent properties due to their chain structures consisting of large paraffin segments linked by a few hydrophilic carboxylate groups. Some of these cements, especially those derived from calcium bases, display energy-absorbing qualities under compressive stress. These cements do not inhibit the polymerization of resin based dental materials (as do eugenol based cements) and, in fact, can be formulated to yield strong hybrid composite cements. The calcium hydroxide based cements have low solubilities and enhanced hydrolytic stability yet provide an alkaline environment which may promote secondary dentin formation. They may find utility as $Ca(OH)_2$ cavity liners, endodontic sealers, etc. Further details on the properties of these cements are contained in the abstracts and microfilmed papers presented at IADR meetings in 1984 and 1985 and at the 10th Annual Meeting of the Society for Biomaterials in Washington, DC, 1984 [33-35]. An invited talk on the properties of hydrophobic, energy absorbing dimer acid cements was given at the Dental Materials Conference at St. Andrew's, Scotland, UK, September 18, 1985.

PROGRESS REPORT

This particular phase of our general program to develop cements of improved durability resulted in strong, tough DA/ZnO cements of low solubility, similar DA/MgO cements, and DA/$Ca(OH)_2$ cements having improved dimensional stability, low water solubility, enhanced mechanical strength and esthetics superior to ZOE cements and, in some formulations, with comparable radiopacity. Strong, esthetic cements from DA/$Ca(OH)_2$ modified with MgO can have various degrees of radiopacity by use of fillers such as radiopaque glass, titanium oxide and zirconium compounds. Dilatometric measurements indicate that these cements generally are low shrinking. In some cases, volumetric expansion on setting occurs suggesting that these cements have the potential to reduce microleakage. Details of this study were presented at the 1985 AADR/IADR meeting.

By proper selection of the base/filler components DA and TA cements with various degrees of translucency can be prepared. Some of these cements harmonize well with the appearance of enamel suggesting their potential for use as an esthetic, intermediate restorative material. For example, translucent cements resulted from using calcium base powders (e.g. $Ca(OH)_2$) with fillers such as fumed alumina, pyrogenic silica, tricalcium phosphate ($Ca_3(PO_4)_2$), composite vitreous fillers and various other optically compatible fillers. With magnesium base powders (e.g. MgO) or mixed $Ca(OH)_2$-MgO powders less translucent, but stronger and less soluble cements are formed. Zinc base powders (e.g. ZnO), as expected, yield opaque cements. The versatile nature of DA and TA cements suggests a wide variety of dental application. Two manuscripts have been prepared for publication.

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

Overview (filler)

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

A variety of types, shapes and sizes of fillers have been used in dental composites, e.g., quartz, fused silica, borosilicate and aluminosilicate glasses, silicon nitride, calcium silicate, calcium phosphates, aluminum oxide, metals, etc. In addition, submicron fillers such as precipitated or pyrogenic silicas (0.14-0.007um) averaging 0.04 um 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 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/inorganic, macrofillers are made from pulverized, prepolymerized composites derived from the silanized, microfine fillers and the same or similar monomer system. 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 um, but usually 3-50um), microfilled composites have a smoother, more easily polishable surface texture which may reduce the adherence of plaque and stains. On the other hand, they have lower elastic 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 (and actually improving) other properties. Some of the newer hybrid composites have a multimodal dispersed phase consisting of different types, shapes and sizes of fillers.

In addition to silanization, another 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. [36-37] 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 conducive to optimal packing efficiency. New techniques that significantly increase filler loadings have recently been developed. [38]

Overview (Interfacial Bonding Phase)

Although they are only minor components of resin based dental restorative materials, interfacial bonding agents exert profound effect on the durability of these 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. Alkoxysilances 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.

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. 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 by silanized composites.

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

Phase II - Development of Improved Interfacial Bonding Phases for Composites and Cements

Objective 1

Develop improved coupling systems for fillers by integral blending, dual silanization and other bonding techniques.

PROGRESS REPORT

A study to assess the relative merits of integral blending of silane coupling agents in composites versus their prior application onto fillers has been initiated. Preliminary results with A-174 dissolved in a BIS-GMA resin paste indicate that in situ silanization occurs over a relatively short period (~2-3 days) and that such cured composites have about the same DTS values as similar composites prepared with presilanized fillers. A second study is in progress to assess the coupling efficacy of other commercially available silane agents, e.g. 3-N,N-dimethylaminopropytrimethoxysilane, 3-DMAPS, predicated on its radical-forming reductive interaction with camphoroquinone (CQ) in visible light activated composites, and 3-mercapto-propytrimethoxysilane (3-MPS) which may bond to the resin by chain transfer reactions. Preliminary results indicate little, if any, coupling of phases occurs using 3-DMAPS. Also when dissolved in the resin phase it is a poor photoreductant for CQ. Similarly, only modest coupling with 3-MPS has been observed as measured by comparative DTS measurements using unsilanized glass composites as a control. Dual silanization studies are in progress with these and other types of silane agents.

Objective 2

Formulation of composite or cement systems with various fillers treated with the best new or binary coupling agents. This work is deferred until the completion of Part 1 of Phase II.

Objective 3

Determination of physical, chemical or mechanical properties as appropriate. Utilize analytical techniques (e.g. HPLC, thermal analysis, etc.) as required to assess the type and degree of silanization. Work on this part also is deferred.

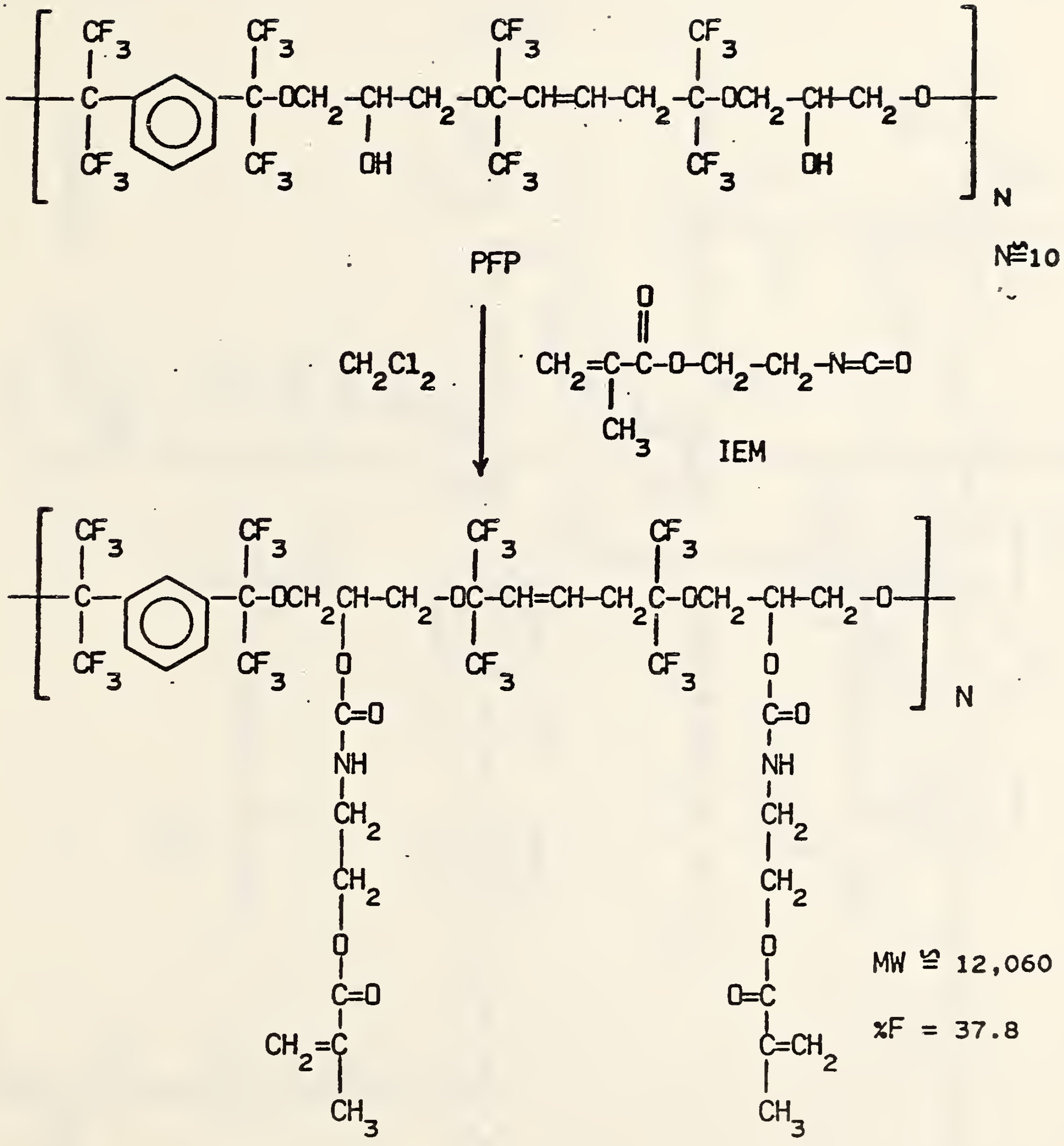


Figure 1. SYNTHESIS OF PFUMA

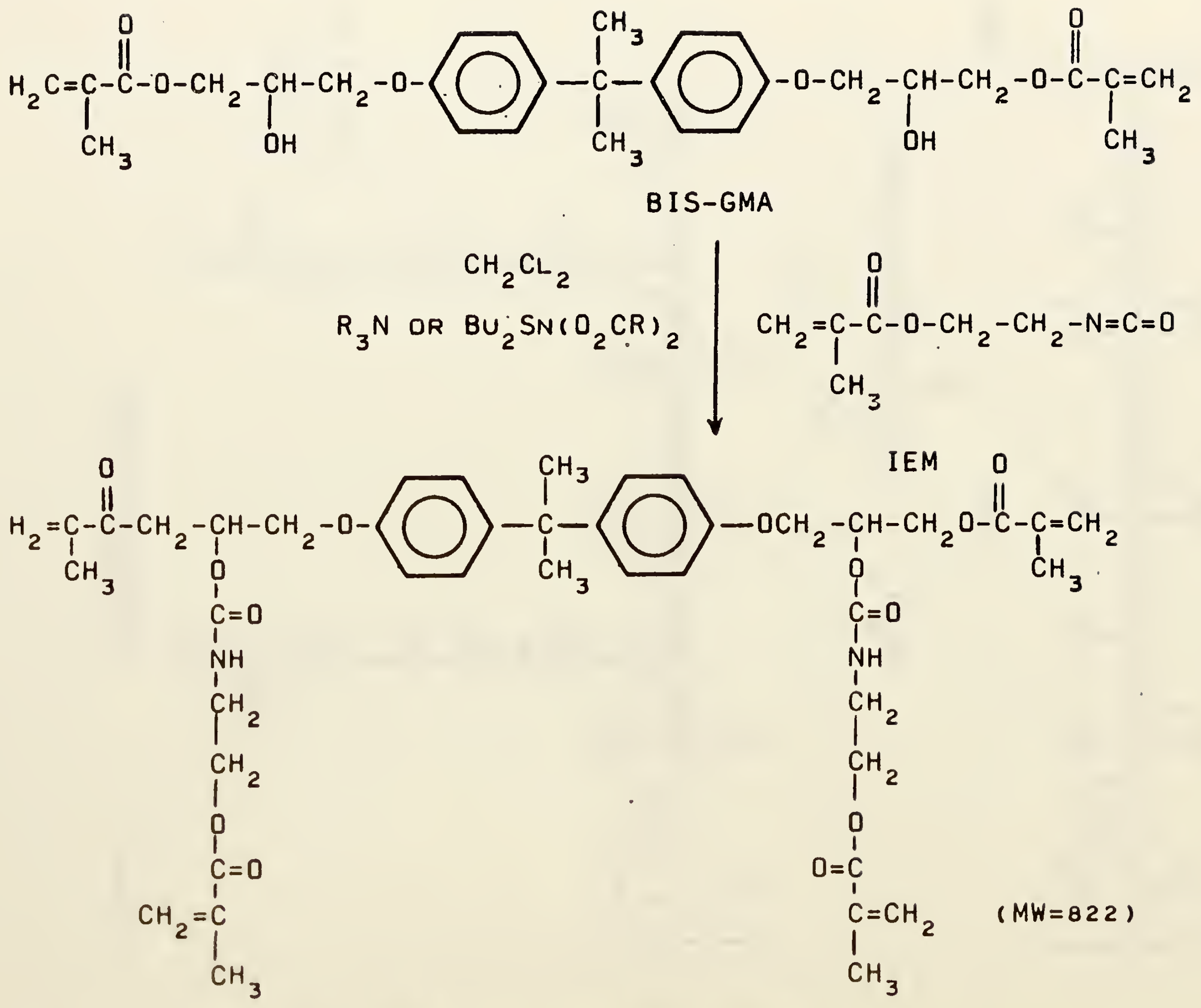


Figure 2 SYNTHESIS OF BIS-GMA/2-IEM

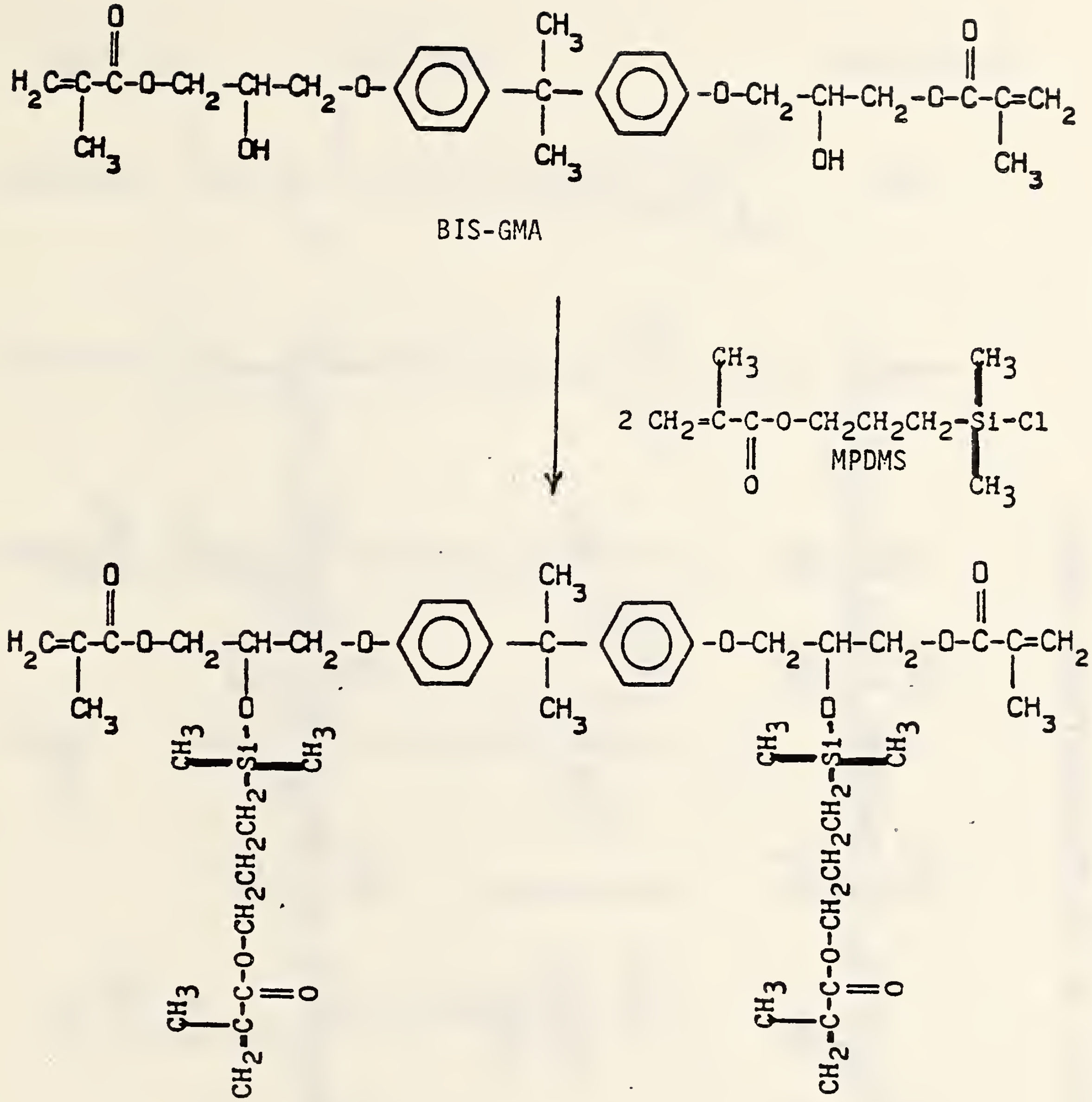


Figure 3 <u>BIS-GMA/MPDMS</u>

SYNTHESIS OF POLYMETHACRYLATE (PFMA)

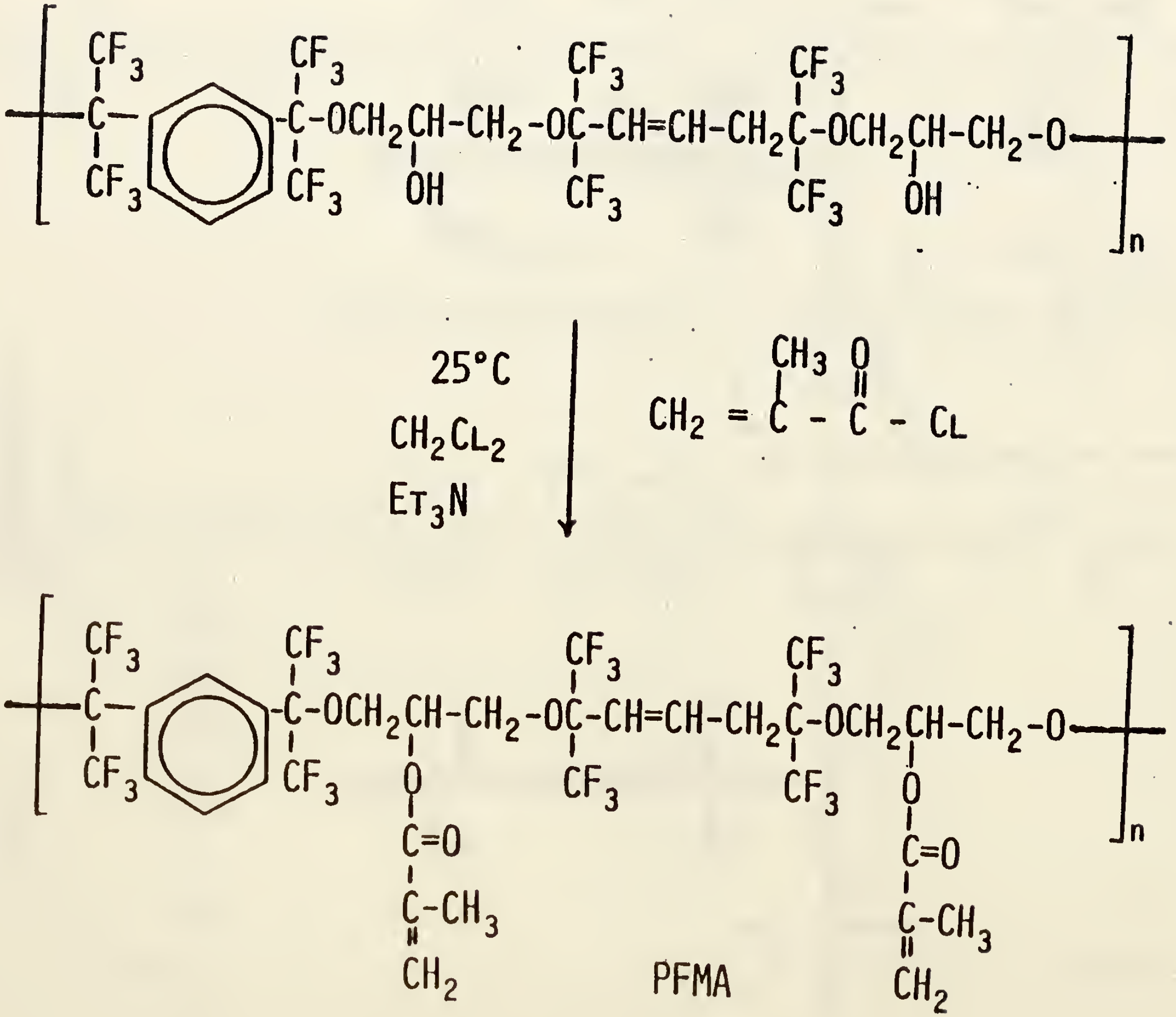


FIGURE 4

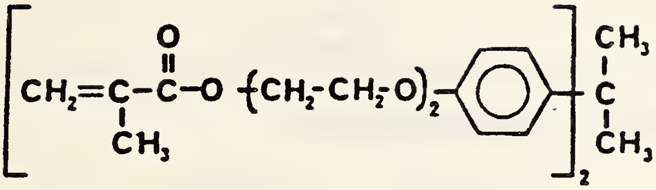
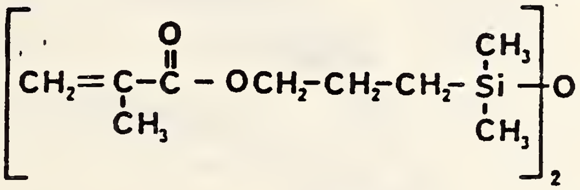
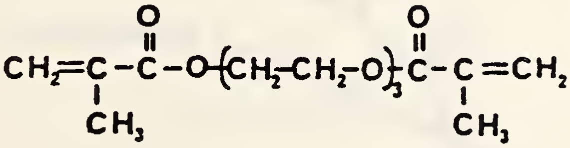
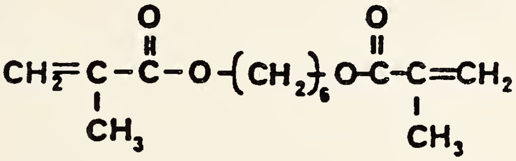
Acronym	DILUENTS	Mol.Weight
EBPADMA		540
Bis-MPTMS	 $[CH_2=C(CH_3)-C(=O)-OCH_2-CH_2-CH_2-Si(CH_3)_2]_2O$	387
TEGDMA	 $CH_2=C(CH_3)-C(=O)-O(CH_2-CH_2-O)_3C(=O)-C(CH_3)=CH_2$	286
HMDMA	 $CH_2=C(CH_3)-C(=O)-O(CH_2)_6O-C(=O)-C(CH_3)=CH_2$	254

Figure 5 DILUENT MONOMERS

Figure 6

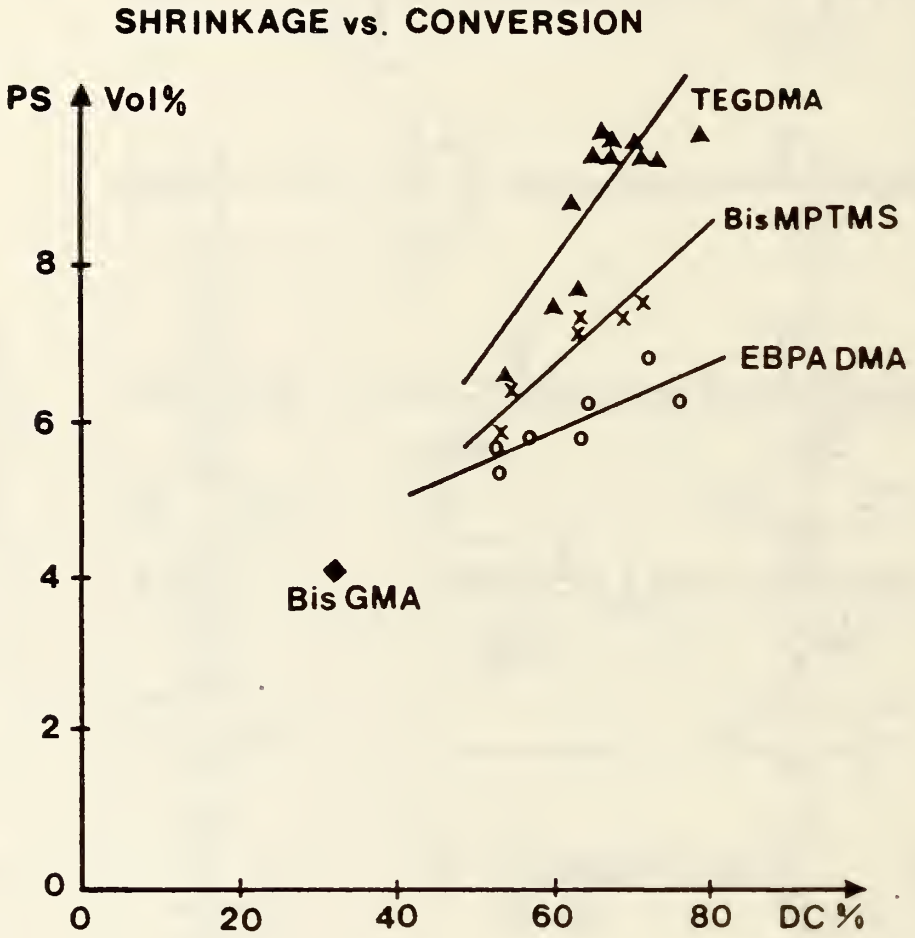

SHRINKAGE vs. CONVERSION
PS
Vol%
TEGDMA
BisMPTMS
EBPA DMA
Bis GMA
8
6
4
2
0
0
20
40
60
80
DC %

TABLE 1

COMPOSITION AND PROPERTIES OF POLYFLUORORESIN BASED COMPOSITES

Resin Composition (wt %)	Polym. Mode, Setting Time (Min)	P/L Ratio (Type of Filler)	24-Hour Strength DTS	Water Sorption (mg/cm^2)	Percent Volume Contraction After 24 hours
PFUMA (67.4) HMDMA (31.7) CQ (0.2) 4-EDMAB (0.7)	VLA	3 (Fused Quartz)	47	0.21	2.8
PFUMA (69.1) BIS-MPTMS (30.0) CQ (0.2) 4-EDMAB (0.7)	VLA	3 (Fused Quartz)	45	0.20	2.3
Commercial Composites	VLA		25-55	0.30-0.80	2.8-4.3

VLA = visible light activation

TABLE 2 MONOMERS USED IN THIS STUDY

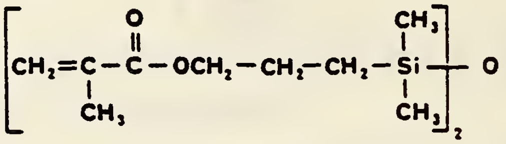
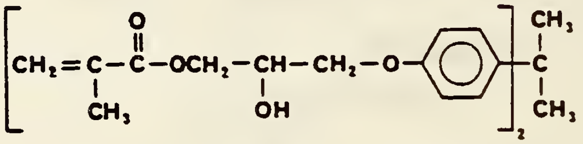
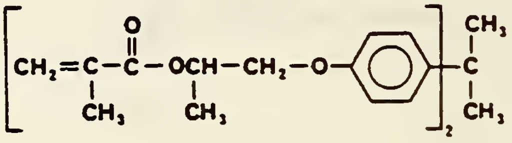
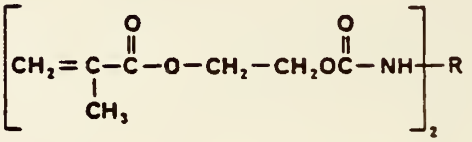
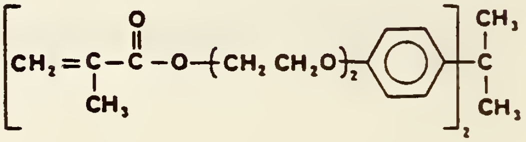
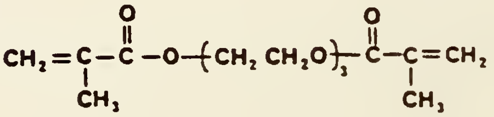
ACRONYM	CHEMICAL STRUCTURE	MOLECULAR WEIGHT	SOURCE
BIS-MPTMS	 $\left[CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-OCH_2-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{Si}}\right]_2O$	387	PETRARCH SYSTEMS, INC BRISTOL, PA
BIS-GMA		512	FREEMAN CHEMICAL PORT WASHINGTON, WI
BIS-IPMA		480	ESPE GMBH, W. GERMANY
UDMA	 $\left[CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2O\overset{O}{\overset{\|}{C}}-NH\right]_2R$	--	DETREY AG ZURICH, SWITZERLAND
EBPADMA		540	ESSCHEM ESSINGTON, PA
TEGDMA	 $CH_2=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-O-(CH_2CH_2O)_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{C}=CH_2$	286	"

TABLE 3

PHYSICAL PROPERTIES OF COMPOSITES MADE WITH SILOXANE-CONTAINING RESINS

Type of Base Resins	Content of BIS-MPTMS (wt %)	Powder/Liquid Ratio	Diametral Tensile Strength MPa (Std Dev)	Compressive Strength MPa (Std Dev)	Water Sorption mg/cm^2 (Std Dev)
BIS-GMA	0	3	47 (1)	212 (20)	0.76 (0.06)
	30%	5	49 (1)	243 (5)	0.43 (0.03)
	50%	6	43 (2)	234 (15)	0.31 (0.04)
BIS-IPMA	0	5	45 (3)	242 (17)	0.13 (0.06)
	30%	5	40 (3)	220 (12)	0.12 (0.06)
	50%	6	43 (2)	193 (11)	0.10 (0.06)
UDMA	0	4	50 (3)	235 (18)	0.49 (0.01)
	30%	5	47 (3)	240 (20)	0.41 (0.06)
	50%	6	40 (4)	200 (21)	0.25 (0.02)
EBPDMA	0	4.5	50 (2)	228 (17)	0.27 (0.06)
	30%	5	45 (1)	216 (35)	0.24 (0.01)
	50%	5.5	40 (2)	218 (17)	0.17 (0.05)

TABLE 4

EFFECT OF BIS-MPTMS VS TEGDMA ON PROPERTIES OF BIS-GMA BASED COMPOSITES

Composition of Resin	Powder/Liquid Ratio	Diametral Tensile Strength, MPa (Std Dev)	Compressive Strength, MPa (Std Dev)	Water Sorption mg/cm^2 (Std Dev)
100% BIS-GMA	3	47 (1)	212 (20)	0.76 (0.06)
BIS-GMA 70%/TEGDMA 30%	4	47 (6)	239 (16)	0.67 (0.10)
BIS-GMA 70%/TEGDMA 30%	5	56 (2)	287 (27)	0.55 (0.05)
BIS-GMA 70%/BIS-MPTMS 30%	4	45 (5)	220 (23)	--
BIS-GMA 70%/BIS-MPTMS 30%	5	49 (1)	243 (5)	0.43 (0.03)

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2. Resin Based Dental Composites An Overview, Proceedings of the 2nd International Conference on Polymers in Medicine, Biomedical and Pharmaceutical Applications, Capri, Italy, (in press) (1985)

Manuscripts under review (WERB)

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

2. Effect of a Polythiol on the Degree of Polymerization of Resins, S.Venz and J.M. Antonucci.

3. Non-aqueous Polycarboxylate Cements Based on Dimer and Trimer acids, J.M. Antonucci, D.J. Dudderar, J.W. Stansbury and S. Venz.

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

5. Synthesis of a Polyfluorinated Prepolymer Multifunctional Urethane Methacrylate, J.M. Antonucci, J.W. Stansbury and S. Venz.

6. Esthetic, Non-brittle Dental Cements Based on Dimer Acid, D.J. Dudderar and J.M. Antonucci.

7. Evaluation of Sioxane-containing Dental Composites, J.S. Kuo, J.M. Antonucci and W. Wu.

Invited talks

1. Fluoropolymer Applications in Dental Materials, Fluoropolymer Workshop, Naval Research Laboratory, Washington, D.C., Feb., 1984.

2. Resin Based Dental Composites. An Overview, 2nd International Conference on Polymers in Medicine, Biomedical and Pharmaceutical Applications, June, 1985, Capri, Italy.

3. Low Surface Energy Dental Composites From Polyfluorinated Prepolymer Multifunctional Methacrylates, 2nd International Conference on Polymers in Medicine, Biomedical and Pharmaceutical Applications, June, 1985, Capri, Italy.

4. Properties of Hydrophobic, Energy-Absorbing Cements, Dental Materials Conference, St. Andrews, Scotland, Sept. 1985.

IADR/AADR/1985

1. Synthesis of a polyfluorinated prepolymer multifunctional urethane methacrylate, J.M. Antonucci, J.W. Stansbury and S. Venz.

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

3. Degree of cure and polymerization shrinkage of photoactivated resin based materials, S. Venz and J.M. Antonucci.

4. Wear and microhardness of ionomer cements, J.E. McKinney, J.M. Antonucci and N.W. Rupp.

5. Detection of lead in human teeth by exposure to aqueous sulfide solutions, A. Sugawara, J.M. Antonucci and G.C. Paffenbarger

6. Esthetic, non-brittle dental cements based on dimer acid, D.J. Dudderar (Hatton award competition - J.M. Antonucci, Proctor)

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

General Overview - This part of the annual report includes descriptions and results of experimental procedures used by us (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 vitro wear of these materials. The results from these studies are expected to facilitate the development of improved prototype composite restoratives here and at other laboratories.

This task is divided into the following sections:

A. Wear and Durability Assessment of Composite Restoratives

Phase I. Experimental composites with flexible chain polymers
Phase II. Ionomer cements - conventional
Phase III. Ionomer cements - metal filled

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

Phase I. Torsional rheometer measurements

A. Wear and Durability Assessment of Composite Restoratives

Background

From microdefect analyses [1] on in vivo worn restoration biopsies, environmental-generated damage was observed [2] on both occlusal and nonstress-bearing surfaces of composite restorations. Accordingly, the intraoral chemistry is believed to play a large role on the in vivo degradation of these materials. For this reason a relevant wear test should include the influence of a simulated intraoral environment. Accordingly, the wear test specimens are preconditioned in appropriate liquids prior to wear testing. Since dental composites comprise two major components, polymer matrix and inorganic reinforcing filler, relevant preconditioning media were chosen which have damage potential to these components.

Previous work at NBS has shown that the in vitro wear resistance and microhardness of dental composite specimens preconditioned in organic food-simulating liquids [3] are commensurate with the extent of solvent-induced damage. [4,5] As the solubility parameter of the solvents was varied by selecting appropriate food-simulating liquids, the wear resistance and hardness minimized at a solubility parameter value corresponding to that of the matrix polymer. Accordingly, the results suggest the selection of matrix polymers having solubility parameter values out of the range of those of liquids encountered intraorally.

During this reporting period a manuscript describing this work was prepared and approved for publication by the Journal of Dental Research.

Increasing the degree of cure of the matrix polymer by elevating the cure temperature improved the wear resistance of the composite specimens. [6,7,8] A higher degree of cure produced a more rigid and closely packed polymer matrix, which, in turn, inhibited the diffusion of liquid penetrants capable of producing surface damage. Since elevating the cure temperature by a sufficient amount in situ is considered to be impractical, an alternative was to develop a flexible-chain polymer which will reach a sufficiently high degree of cure at the in situ temperature, 37 °C.

Our work on the influence of intraoral acids, and even water, on the degradation of certain commercial composites has revealed decreases in microhardness and wear resistance. [9] More severe consequences were observed on composites employing modified glass fillers to obtain radiopacity than on those employing pure silica fillers. The failure mode results from stress corrosion of the filler causing a breakdown at the interface. For this reason we have turned our attention to ionomer cements which have tight ionic bonds between polymeric matrix and glass filler resulting in a more continuous interface.

The cure process of the 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 ionomer cements.

Objective

The objective of this task is to identify the in vivo wear and degradation mechanisms of dental composite restorations. The results, when correlated with in vivo tests, facilitate the development of new dental composite materials.

PROGRESS REPORT

Phase I

Experimental composites with flexible-chain polymers. --Microhardness measurements have been made on several composites employing flexible-chain polymers and these polymers in neat form. A large portion of this work was done by a research associate from Dentsply International. As with the more conventional composites, preconditioning was done in appropriate organic liquids. With new composites and their polymers, of which most were siloxane-containing or fluorinated copolymers, the microhardness of the preconditioned specimens minimized at lower solubility-parameter values than that for the more conventional composites and their polymers, e.g., BIS-GMA.

Wear measurements were initiated on an experimental composite containing a 70/30 PFUMA/BIS-MPTMS[1] matrix polymer. The specimens were preconditioned in 100% ethanol and in pure water. Previous microhardness measurements over a solubility-parameter scan revealed a minimum corresponding to the solubility parameter of pure ethanol. The degree of softening determined from the Knoop Hardness Numbers of the 100% ethanol-preconditioned specimens was larger than that of any dental composite we have tested. There was no effect, however, on the water-preconditioned specimen.

On the other hand, the initial wear was very small and about the same for both kinds of preconditioning. Although the steady-state wear was large, it was about the same for both cases. Even though the composite was subject to extreme softening in ethanol, the wear was stable. This paradox, apparently, results from the high degree of crosslinking in this polymer and its more rubberlike character which allows softening, but limits decomposition or breakdown during wear.

Phase II

Ionomer cements - conventional. -- Wear and microhardness measurements [10] were made by NBS on preconditioned commercial specimens of essentially the same content. The preconditioning media were air, water, and 0.02 N lactic acid. As usual, the preconditioning period was one week. With the air-preconditioned specimens, the hardness increased by nearly a factor of three, and wear studies were essentially impossible due to the catastrophic failure resulting from brittle fracture of the dehydrated specimens. With the lactic-acid preconditioning, the hardness fell markedly with a corresponding decrease in wear resistance. Since lactic acid is generated from plaque formation, it is intraorally omnipresent in many people. This kind of chemical instability is a serious limitation to the application of ionomer cements as presently formulated.

Phase III

Ionomer cements - metal filled. -- Wear and microhardness measurements were extended to include a commercial silver-modified ionomer cement. As with the more conventional ionomer cements, the hardness declined the most during the lactic acid preconditioning; however, the differences between the results from different preconditioning media were less. With both the water and lactic acid treated specimens the wear resistance increased considerably over that of the more conventional ionomer cements. The silver appears to provide a lubricating effect. On the other hand, the susceptibility to brittle fracture during wear does not appear to be improved by

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[1] For more details on the formulations and synthesis of this polymeric system, see Part I, Section E.

the addition of combined silver. SEM microdefect analysis revealed some damage to the silver-filled ionomer cements preconditioned in 0.02 N lactic acid. The extent of damage was not as much as that observed for the more conventional ones.

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

Background

As stated in the last section, dental composite restorations may be made more durable by increasing the degree of cure of the matrix polymer. In addition, we have determined that both the in vitro wear resistance and micro-hardness are increased by increasing the degree of cure through elevation of the cure temperature, T_c. [6,7,8] Since this method of increasing the degree of cure is considered to be impractical for in situ placed restorations, an alternative must be considered.

The problem with free-radical cured systems, of which BIS-GMA is an example, is depicted in Figure 1 where the glass transition temperature, T_g, or the degree of cure, x, is plotted against cure time at the isotherm, T_c. As the cure proceeds, T_g or x will increase until T_g approximates T_c at which the cure essentially terminates prematurely. [11] The limited degree of cure results from an increase in molecular viscosity, which prevents reactive groups from becoming proximate. Since these groups cannot react with each other to form crosslinks, the degree of cure is essentially limited at a terminal value, and the pendant vinyl groups can have a plasticizing effect on the matrix and serve as potential sites for oxidative attack.

From Figure 1, it is evident that the degree of cure may be increased by either increasing T_c or decreasing $T_{g\infty}$, the value of T_g corresponding to a completely cured system for which x = 1, to make the difference $T_{g\infty} - T_c$ smaller. Since in clinical applications increasing T_c is impractical, the alternative of the polymer is to decrease $T_{g\infty}$. This procedure is more difficult in that it involves nontrivial changes in chemical structure for which more detailed narratives are given in Part I, Section E. These involve silaxane-containing copolymers and fluorinated copolymers to produce flexible chains. In addition the solubility parameters of these polymers are expected to have lower values than those of the typical dental polymer. This, in turn, is expected to reduce the interaction with the organic liquids present in foods.

Objective

The objective of this task is to determine the glass-transition temperature of selected dental polymers as a function of cure temperature.

PROGESS REPORT

Phase I

Torsional rheometer measurements. -- T_g measurements [12] have been made on pure BIS-GMA and 70/30 BIS-GMA/TEGDMA polymers in collaboration with a guest worker from The Taiwan National University using a Weisenberg Rheogoniometer. This viscoelastic technique employs forced vibration in torsion at constant frequency (in this case 1.9 Hz). From a temperature scan, T_g is determined from the temperature at which the energy dissipated is a maximum. For example, at a cure temperature of T_c = 183 °C, the measured T_g is about 178 °C for both polymers. This value of T_g is much less than $T_{g\infty}$ because a complete cure is still not obtained even at this elevated temperature. For our application, we desire a polymer with $T_{g\infty}$ at about 90 °C for which $T_{g\infty}-T_c$ = 53 °C with T_c here, the <u>in situ</u> cure temperature, 37 °C. A value of $T_{g\infty}$ too high produces an undercure. A value too low produces a rubber-like material, which is not useful for restorative application. Thus the determination of T_g is useful, or perhaps even essential, to optimize these materials with respect to long term <u>in vivo</u> durability.

This determination also gives the shear moduli above and below T_g, which are useful for development of these materials.

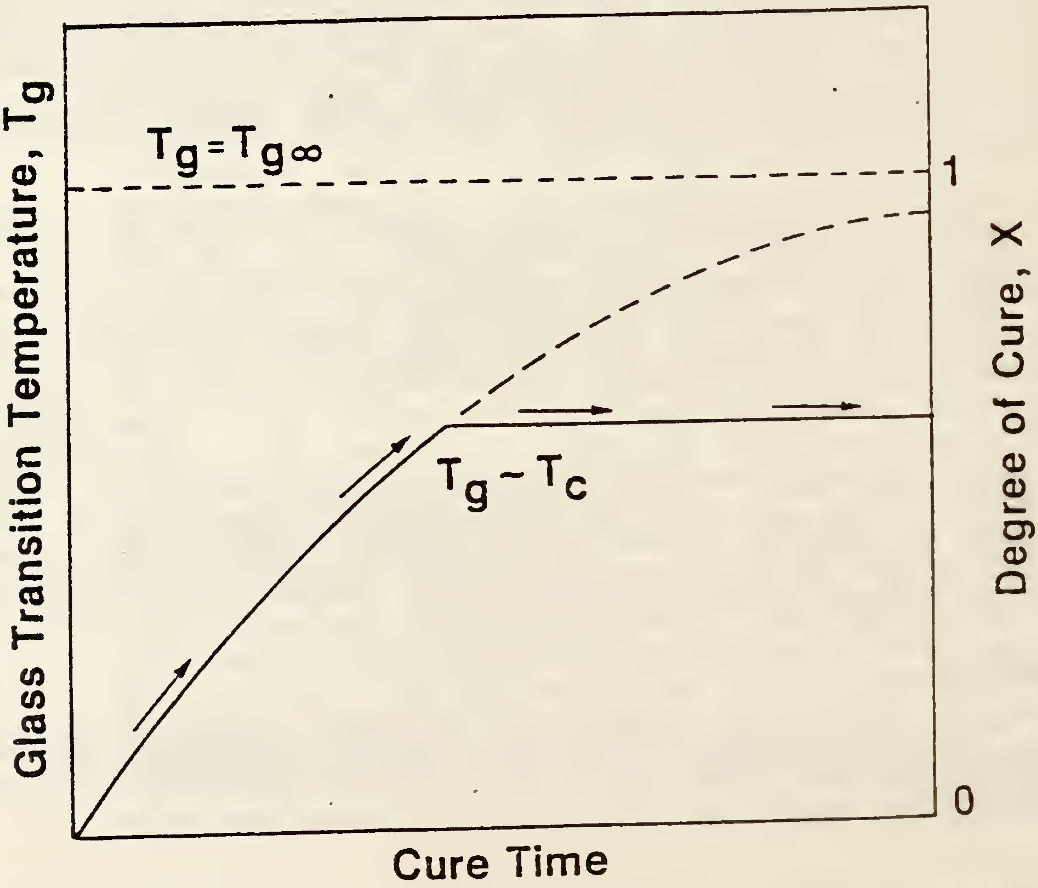

FIGURE 1. Schematic variation of the glass transition temperature T_g or degree of cure x with cure time. When T_g=T_c, where T_c is the cure temperature, the curing process terminates.

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Environmental Damage and Wear of Dental Composite Restoratives, J.E. McKinney, Proc. Intl. Symp. Resin Based Posterior Materials, Mullet Bay, St. Maarten, Neth. Ant., ed. D.C. Smith and G. VanHerle, Jan. 1985.

Manuscripts Accepted for Publication

Chemical Softening and Wear of Dental Composites, J.E. McKinney and W. Wu, J. Dent. Res. (in press)

Manuscripts Under Review

An *In Vitro* Comparison of the Wear Rates of Acrylic, IPN, and Microfilled Denture Tooth Materials, D.J. Whitman, J.E. McKinney, R.W. Hinman, R.A. Hesby, and G.B. Pelleu, Jr., Submitted to J. Prosth. Dent. for publication.

Invited Talks

Environmental Damage and Wear of Dental Composite Restorations, J.E. McKinney, Proc. Intl. Symp. on Posterior Composites, Mullet Bay, St. Maarten, Netherlands Antilles, eds. D.C. Smith and G. VanHerle, Jan. 1985. (Corresponding publication entered separately).

Contributed Talks

Wear and Microhardness of Ionomer Cements, J.E. McKinney, J.M. Antonucci, and N.W. Rupp, IADR Abstracts 64, No. 1767 (1985)

Glass Transition Temperature of Dental Composite Resins, W. Wu and C.C. Yu. IADR Abstracts 64, No. 487 (1985)

III. DENTAL ALLOYS AND CERAMICS (AND METROLOGY)

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

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

PROGRESS REPORT

Overview

Residual stress from the porcelain firing cycle is considered to be a major factor leading to failure of porcelain fused-to-metal restorations. This stress has its origin in the differences in thermal expansion which exist between porcelain and alloy throughout the firing temperature range. Other properties which also affect the build up or retention of stress include the thermo-plastic properties (primarily of the porcelain), thermal conductivity, and temperature-dependent elastic moduli. Geometric variations in restorations are also contributing factors. This study was undertaken to define the thermo-mechanical stress compatibility in terms of those parameters.

Accomplishments

The objective of this part of the investigation was to explore the potential of using the gap of a procelain veneered split metal ring as a means for determining the thermal-stress compatibility between the porcelain veneer and the metal substrate. The change in gap upon cooling from the veneering temperature is the effect measured and desired. For this purpose several finite-element models (FEM's) had been developed, each to assess in a preliminary manner the material properties required and the graphic grid and computer program necessary to provide good insight into the compatibility problem. Earlier work reported on [1,2] indicated that the porcelain ring composite would be highly indicative of viscous relaxation behavior of the porcelain (two porcelains with nearly the same values of α, the coefficient of thermal expansion, had shown greatly different gap changes). It was considered necessary to obtain the temperature dependence of the elastic modulus of several porcelain and alloys in order to refine calculations of gap changes. (These changes are then to be correlated with experimentally-determined values. Ultimately, it is expected that tables of properties and stress, etc., or simplified regression equations or other techniques can be developed which will describe thermal stress compatibility, with the split ring serving as the experimental check on the methods employed. It should be noted that the resultant description of compatibility should be generally applicable for any veneering process using thermal techniques provided the critical material properties are adequately described...one intent was to confirm what the critical properties are).

Phase I

During the previous period, progress had been made in determining the temperature-dependent elastic moduli for three alloys and two porcelains. One manuscript (see publications #1)* has been published in this period and another (see manuscripts in review**) has been submitted for publication.

Also determined were the surface temperature differences between porcelain and metal during cooling of a split ring having thicknesses of 0.8 mm of porcelain and 0.5 mm of metal. The maximum temperature difference was 35 °C, reached shortly after cooling from 980 °C.

Phase II

These data, along with previously obtained results on temperature-dependent viscosities of the porcelains [3] and their thermal expansions [1] will be used in a refined finite element program (under construction) on analysis of gap change, (and resultant stresses) as functions of these parameters and cooling conditions.

Phase III

Finalize material input parameters for split ring computer program and fine tuning for match with experimental results. Planned for FY 86.

Phase IV

Devise simple analytical representation of split ring stress-strain calculations, if possible.

Phase V

Examine results of FEM vs 2-dimensional theory developed by Scherer. FY 87.[4]

B. Porcelain-Alloy Compatibility (Bonded System Strength)

PROGRESS REPORT

Overview

Numerous tests have been proposed by others [5, 6, 7, **for example]** for the purpose of evaluating the porcelain-metal bond strength (PMBS). Some are qualitative in essence, others attempt to test in shear even though brittle materials fail in tension (porcelain and the nonmetallic interface are brittle). Often, the test designs involve curved or sharp boundaries between the porcelain and the metal, further complicating any analysis (qualitative or quantitative) because of the crack initiation aspects of such stress raisers.

In an attempt to overcome the forementioned difficulties, a bending beam composite (BBC) specimen was designed for evaluation. The specimen is prepared to provide all smooth surfaces at porcelain-metal junctions when subjected to the proper bending moment and creates tension at the bond and within the porcelain. Alignment of the specimen is not critical (misalignment by a few degrees about an axis perpendicular to the horizontal plane of the specimen results in only a few tenths of a percent effect on the calculated stress).

Three-dimensional finite element and two dimensional finite-element stress analyses showed good agreement with beam theory analysis.

Accomplishments

Phase I

Test fractures for the BBC were not isolated to only the interface, but were distributed through the porcelain (lying in, near, or 1-2 mm away from the interface. It is apparent that what is really being evaluated is porcelain fused-to-metal system strength; this is also what is clinically important. It also became understood that every other dental porcelain-to-metal bond test in the literature is in reality testing porcelain-metal system strength. With this in mind all fracture data were grouped in cumulative failure plots for each system tested and graphically-distinct differences could be discerned where the simple application of normal distribution statistical analyses revealed none. Because we are dealing with brittle fracture in ceramic materials (by observation...also, the metal is not expected to fail as the lowest metal-yield strength is ~3X the tensile strength of the porcelains) Weibull statistics curve fitting (cumulative failure) is deemed the appropriate approach.
One paper on the feature of specimen design, and stress analyses has been prepared. (See manuscripts in review, #2) It will be submitted for publication with another manuscript which is currently in preparation and deals with the Weibull analysis. It is considered important to publish these two papers together as each lends substance to the other. For this reason the first manuscript has not yet been published.

The Weibull method has been chosen to provide more convenient and significant differentiation between porcelain-metal bonded systems. It is proposed to explore two- and three-parameter Weibull plots for fitting of fracture data. Generally, according to Weibull for a large sample of data, the probability of failure at a given stress level P(σ) may be represented by:

$$P(\sigma) = 1 - e^{\left(\frac{\sigma - \sigma_i}{\sigma_o}\right)^m}$$

where σ is the level of stress

σ_o is a characteristic stress

σ_i is a threshold stress (0i >0)

m is a shape or distribution parameter.

As an example, let $\sigma_i = 0$. Then two porcelains with the same σ_o, but with different values of m would plot as shown in figure 1.

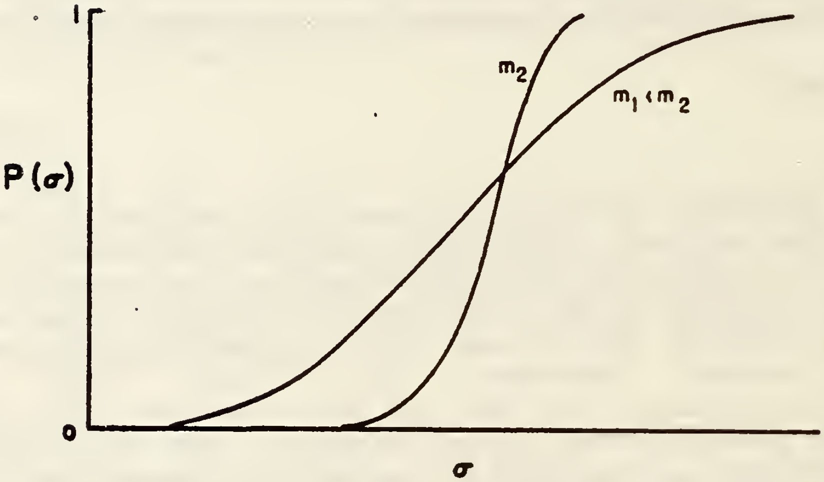

Figure 1

The average, or mean values of these two porcelains would be nearly the same, (this is slightly oversimplified, but this approximation is used to demonstrate the usefulness of the Weibull approach). Hence, these systems would be virtually indistinguishable by simple normal distribution statistical analysis, yet it is clear that system #1 (Figure 1) is more prone to failure at lower stresses. This is expected to be of clinical significance. For example, system 1 could be expected to have many more early clinical failures due to the to failures at low stress levels. The application of Weibull analysis could lead to greater understanding and definition of critical parameters for improving dental porcelain-metal systems. Further, the analysis and four-point bend test is not restricted to porcelain-metal systems, it should find applicability for other dental bonded systems, such as enamel-to-resin dentin-to-resin, composite-to-metal and so forth.

Phase II

Determine three dimensional and two dimensional FEM of BBC. This phase was completed in FY 83.

Phase III

Determine theoretical curve fitting methods: exploration of 3-Parameter Weibul analysis. Under investigation...will pursue in FY 86.

Phase IV

Photo elastic study of BBC...to be explored in FY 86 and 87, if deemed necessary.

Phase V

Explore effects of alloy reuse, specimen reuse, annealing of porcelain, immersion in water (or saline solution) on system strength. To be initiated in FY 86.

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

PROGRESS REPORT

Overview

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

Numerous methods have been proposed in the past for determining various aspects of the casting of dental alloys. A number of procedures have been proposed. Asgar [8] described a method using a spiral pattern. The length of spiral that was cast was used to provide a quantitative measure of the ability to cast an alloy. Obtaining consistent, nearly identical patterns with a constant pitch for all spirals and constant diameter could be a difficulty encountered with the use of such a method and would complicate the length-measurement process. Sorensen and Ingersoll [9] used a stainless-steel mold to produce patterns in the shape of a six-spoked wheel with thin web sections between the spokes to indicate fluidity of gold casting alloys., Obtaining a quantitative measure of cast-ability of an alloy is virtually impossible with that pattern, although good qualitative information can be derived. Vincent et al. [10] describe a method for measuring castability by using a pattern with a range of rod diameters. Quantitative and qualitative information is available from this technique, and it does allow for separation of some aspects of castability. This technique also requires a precise measurement of length to ~0.1 mm. Preston and Berger [11] employed a spring-shaped pattern similar to Asgar's while Nielsen and Shalita [12] and Barreto et al. [13] have used various configurations of a wedge; these also require precise and microscopic measurements. Smith et al. [14] studied both castability and fit together using a simulated molar crown scribed with lines for measurements with a traveling microscope. Nielson et al. [15] have developed a razor monitor which is capable of relating effects of variables such as alloy temperature and mold temperature in terms of reproduction of fine detail.

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

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

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

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

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

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

(6) The method should be sensitive to materials, temperature, techniques, or other variables affecting castability.

Accomplishments

Phase I

Statistical and functional representation of castability. One manuscript has been published (Publication #2) entitled "A Technique for Characterizing the Casting Behavior of Dental Alloys". Another manuscript, "Castability of Dental Alloys, Mold and Alloy Temperature Effects", has been prepared and is under internal review.

Phase II

Analysis of Effects of Composition on Castability. The first determinations of this have been made, using data available from the six alloys mentioned in Phase I. The following equation was found:

$$c_{v_t} = K_o + K_1 [Si] + K_2 [B] + K_3 [Cb \times Sn] + K_4 [Al \times Be] + K_5 [Mo \times Mn]$$

Where : K_i = function of mold and alloy temperature
[ ] = concentration of elements

This expression needs further refinement as it is not certain that the terms involving products of elemental compositions are sufficiently independent in each element, that is, some particular compositions appear to be too strongly correlated. Also, to be strictly correct, only one investment should be used for obtaining the castability data whereas 3 were used for the earlier parts of this program. However, at this point, the technique has been demonstrated to be a viable method for analyis. A manuscript (publication #5) on this was prepared for presentation as an invited paper at an International Precious Metals Institute Meeting in Israel, April 1985.

For the six alloys in question, preliminary results have shown the temperature-dependent effects on K_i for B and Si (Figures 2 and 3). Determinations of K_i's will be useful for computer aided design of dental alloys.

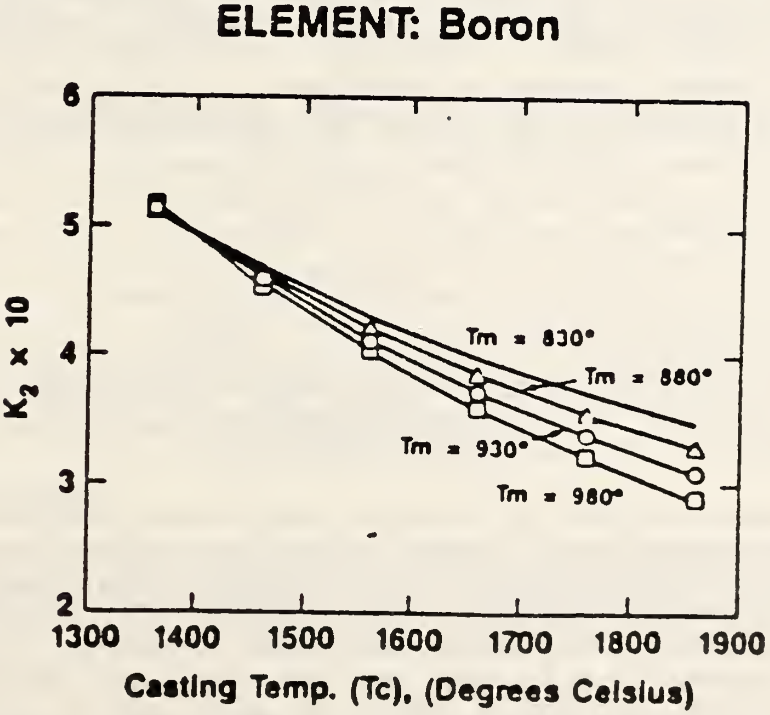

Figure 2: Effect of alloy casting temperature on constant, K_2, (equation 3a, text) for boron. The alloy is a Ni-Cr based alloy.

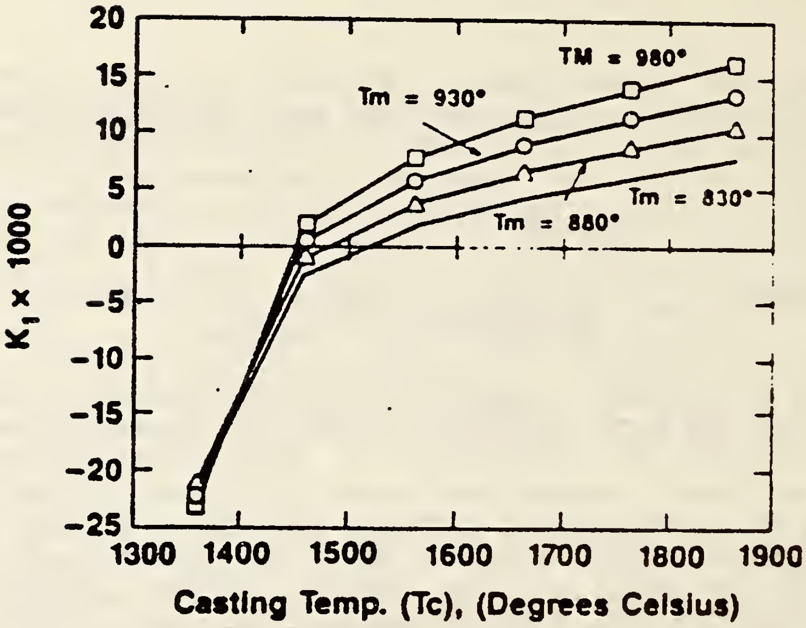

Figure 3: Effect of alloy casting temperature on constant, K_1, (equation 3A, text) for silicon. The alloy is a Ni-Cr based alloy.

Phase III

In order to investigate the effects of investments on C_{vt}, one alloy (from one batch) was cast into several investment batches of the same brand of investment. The results showed that for two different batches of investment, 1 and 2, this previously found equation for the transformed castability value, $C_{v,t}$, is:

$$C_{v,t1} = a_1 + b_1 \; T_A^{1/2} \cdot T_M^2$$

$$C_{v,t2} = a_2 + b1 \; T_A^{1/2} \cdot T_M^2$$

where T_A is the alloy superheat temperature, given by $T_A = T_C = T_S$, and T_C = the casting temperature, T_S = the alloy solidus temperature. T_M = the mold temperature.

In these equations "b" remained unaffected, with the effect of batch showing on the term"a". Hence the temperature dependence of C_{vt} is unaffected by batch variation; (note; however, C_{vt} is changed through changes in the constant, a). This result may prove useful in correcting laboratory procedures, if necessary, when batches are changed and indicates the desirability of maintaining as large a supply of one batch of investment as possible in order to avoid encountering casting problems from changing batches. It is conceivable that C_{vt} might also be used to characterize investments with a standard alloy. A manuscript on preliminary results has been published. [see publication #5]

D. Castability (Accuracy of Fit of Dental Castings)

PROGRESS REPORT

Overview

Because base metal alloys had come into widespread use Eden et al. [16] investigated the reasons for their often producing tight fitting castings. They demonstrated that satisfactory oversized single unit castings could be achieved routinely with a modified investing technique. Although this technique worked with single units centrally located in the investing ring, the question arose as to how well it might work with multiple unit castings. An extension of this study by Hinman and co-workers revealed the conditions under which multiple unit castings produced the best fit. It was found that pattern distortion apparently was greater than mold expansion distortion and that a bench set technique with an all wax pattern system (pattern, prues, runner bars) produced the most consistently accurate dental castings.

In view of these results and early results of Marsaw [17] it appeared that the internal setting expansion of dental investments was lower than and quite different from that obtained from external measurements and run by manufacturers according to ADA measurement techniques. A similar finding of lower internal expansion had been obtained many years ago by Asgar [18] on gypsum investments.

The ballon techniques of Asgar et al. and Marsaw et al. are difficult to set up and monitor and the casting techniques are not sufficiently controllable to separate the effects of many variables on setting expansion. Hence, some preliminary studies using strain gauges were considered for investigating internal setting expansion. It was reasoned that a strain gauge might act very much like a pattern and not begin to change shape until the investment was sufficiently set to deform it. Therefore, it seemed to provide a reasonable approach toward isolating setting expansion from other unknown efforts such as pattern distortion. The strain gauges are small and planar and measure expansion in only one direction.

Accomplishments

One paper on the fit of multiple unit fixed partial dentures was published in this reporting period (publication #4).

Phase I

Preliminary experiments on the use of strain gauges were conducted and the findings published (see publications, #6). These results confirmed the earlier results of Marsaw and of Asgar and their co-workers in that the internal setting expansion was indicated to be much smaller (~0.10%) than manufacturers indicate from their external measurements (~1%)

Phase II

This work will be continued with the following objectives: (a) improve stability and reproducibility of individual strain gauge measurements and (b) examine multidirectional and specific spatial effects.

E. Solderability

PROGRESS REPORT

Overview

The original objective of this work was to examine whether bend or pure-tensile testing was the most effective method for evaluating the strength of soldered joints. Following the work reported on for FY 84 it may be stated now that it is not planned to continue this work beyond that previously reported on as the investigators do not believe that any particular difficulties exist with either bend or tensile testing of soldered joints; hence, there is not considered a need here for development.

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

PROGRESS REPORT

Overview

Although many other properties must be considered in choosing materials for restorations and prostheses two of the primary properties or characteristics to be considered are mechanical strength and durability.

As a necessary adjunct to NBS dental research projects, this group has long maintained various kinds of general purpose test and analysis equipment such as tensile machine and hardness indentors. These are used by researchers to conduct standard tests for strength as well as non-standardized tests of such properties as adhesive strength or the retention strength of prostheses for example. In addition, this group has developed and now maintains several less common devices in support of various projects. These include a mercury filled dilatometer for measuring the volume changes which occur during the setting of restorative materials, apparatus for measuring thermal expansion from room temperature to 1600 °C and apparatus for measuring tensile and shear moduli from room temperature to 500 °C.

Besides these devices, we are developing various test methods. These include a four point bending test for characterization of the strength of bonded dental systems such as porcelain-fused-to-metal and composite to metal, for example, a split ring test characterizing thermo-mechanical capability in veneered systems (such as porcelain-fused to metal, ceramic to ceramic, etc.) and a castability index test to quantify the ability of an alloy to produce complete castings under various sets of conditions.

Objective

The objective of this project was to develop various test instruments and methods to the point that they can be used by researchers for routine measurement. A device for measuring the volume changes which occur on the setting of restorative materials was needed for research in other parts (I and II) of our program. Another section of this effort has involved an investigation of the suitability of using the standard diametral test [19] for evaluating the tensile strength of modern dental composites.

Accomplishments

Phase I

Development of a Recording Dilatometer for Measuring Polymerization Shrinkage

A device described in the literature for measuring polymerization shrinkage was constructed. However, this device was thermally and mechanically unstable, i.e., it required much longer periods (several hours) for the system to stabilize during an experimental run than the time for the polymerization to be completed and the magnitude of the drift was of the same order or greater than that of the expected change in output due to the polymerization.

The problem was solved by replacing the poly (methyl methacrylate) device with a more rigid, less massive one constructed of pyrex glass and by substantially reducing the volume of mercury. Ancillary equipment which had been developed functioned satisfactorily with the new dilatometer. This included a thermostatic air chamber which is stable to ± 0.01 °C linear variable differential transformer device for measuring the volume changes as well as a simple pyknometer for measuring the sample volume. The device has been shown to be sensitive to volume changes of $\pm\ 10^{-5}$ CM^3 and to be stable to within those limits for periods of several hours. The device is now in routine use and several requests for information have been received.

A poster presentation and manuscript describing the dilatometer device were presented at the IADR meeting in March 1985, and a manuscript has been submitted for publication to the Journal of Dental Materials.

This project of development of a dilatometer for measuring polymerization shrinkage is completed. One manuscript on the design of the dilatometer has been submitted for publication (see manuscript in review, #5).

Phase II

Evaluation of the Suitability of Applying the Diametrical Tensile Test for Determining the Tensile Strength of Dental Composites.

During the 1984 meeting of the International Association for Dental Research the question arose among two scientists from the NBS and University of Michigan (UM) dental groups whether the diametrical tensile test [19] remained a valid test method for evaluating the tensile strength of modern dental composites. These composites often contain lower amounts of filler, have different curing systems and modified resin matrices from those in existence at the time of development of Spec. #27. [19]

In a cooperative effort between NBS and UM to test the validity of using the DTT for newer dental composites, four composites were chosen for testing, each having one or more essential difference from all others. It was reasoned that for either a deformable or viscoelastic material, the calculated failure stresses should be strain rate dependent. Hence, forty DTT specimens were prepared at NBS for each composite evaluated (Table #1) and divided into four equal groups for testing at different crosshead speeds (CS) (or strain rates) of 5, 0.5, 0.05, and 0.005 cm/min. Twenty specimens were similarly evaluated at UM.

Test results are given in Table 2. The results for each material were fit to a regression curve of the form $y = A+BX$, where y = the DTS and X = the log CS. Correlation coefficients, r, were also calculated and the "pooled" "t" values were obtained from

$$t = \sqrt{\frac{r^2(N-2)}{1-r^2}}$$

The probability, α, of obtaining a t value equal to or greater than the calculated t was obtained from a table of t values. The results are summarized in Table 3. In the above formulation, N = the pooled number of samples, 40 for NBS and 20 for UM.

From Table 2 we note that from the NBS evaluation significant correlation with log CS exists at the 95 percent confidence level (or better) for materials a, c, d, e and from the UM evaluation for materials d and e. It should be noted that S (the estimate of the standard deviation) is linearly related to the magnitude of the value of Y, Fig. 1. Hence, in order to compare effects between materials it was necessary to transform all data to a parameter, P, which is independent of log CS. Dividing $y = A+BX$ by Y accomplished this; hence, B/Y was compared for each material. Under these conditions it can be seen in (Table 2) that all values of B/Y are less than those for material e, an accepted brittle material. It was; therefore, concluded that each of the materials in question is functioning in a brittle manner, as the effect of log CS on the DTS is less than its effect on the brittle material, e.

Hence, the DTT is a viable method for determining the tensile strength of modern dental composites. One manuscript (see manuscript in review, #4) is in review.

TABLE 2

Parameters resulting from analysis of diametral tensile testing of composites. Regression analysis according to equation $y = A + BX$ and statistical evaluation.

	Material				
Parameters	a	b	c	d	e
NATIONAL BUREAU OF STANDARDS TESTING:					
r	0.32	0.10	0.50	0.48	0.53
Y	36.9 (3.4)	35.6 (4.22)	53.3 (5.3)	59.6 (6.2)	6.7 (1.1)
B	1.02	1.09	2.71	2.96	0.58
$B/Yx10^2$	2.76	3.05	5.09	4.97	8.7
t	2.05	0.62	3.55	3.37	3.85
α	0.05	0.5	0.001	0.005	0.001
UNIVERSITY OF MICHIGAN TESTING:					
r	-0.14	-0.31	0.28	0.49	0.58
Y	32.4 (4.0)	31.7 (3.7)	49.1 (4.9)	51.7 (4.11)	4.3 (0.71)
B	-0.51	-1.0	1.24	1.99	0.43
$B/Yx10^2$	-1.6	-3.2	2.5	3.9	10.1
t	6.60	1.38	1.24	2.38	3.02
α	0.5	0.2	<0.2	<0.05	<0.01

r = correlation coefficient
Y = mean value of all values of where Y is the breaking strength of individual specimens tested at various crosshead speeds with standrd deviation in parenthese.
B = regression coefficient
t = t value from standard t tables for confidence level α, for the degrees of freedom and standard deviation applicable
α = significance level

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* Invited and scheduled, unable to present due to poor health at that time.

** Invited, paper presented, but unable to attend due to poor health at that time.

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Diametral Tensile Strength and Dental Composites, R.G. Craig, R.W. Penn and J.A. Tesk, March 1985.

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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 systems potentially applicable to other composite applications, e.g., durable resin matrices, stronger more durable coupling between fillers and resins and improved reinforcement by defining the types, compositions 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 spectrocopy, 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 by wear and hardness measurement techniques, 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 of clinical results on wear and failure of composites with laboratory test data via a time to failure analysis. Metrology and analysis constitutes the underlying theme of investigation into porcelain-metal system, casting of dental alloys and expansion of 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")."

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*
adhesion; castability; dental alloys; dental casting alloys; dental cements; dental composites; dental materials; dental restoratives; wear and degradation of composites.

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