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U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, ***Secretary***

Luther H. Hodges, Jr., ***Deputy Secretary***
Jordan J. Baruch, ***Assistant Secretary for Productivity, Technology, and Innovation***

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

TABLE OF CONTENTS

ABSTRACT

Significant accomplishments in the field of dental research for the past year include:

(1) Development of more efficient, less toxic polymerization accelerators. Biocompatible 4,4,N-diethylaminophenylacetic acid, which is reactive at four-fold reduced concentration relative to currently used amines is very promising.

(2) Raman, IR and ^{13}C NMR spectroscopy and DSC are being compared for investigation of dental resin polymerization.

(3) Solvent carrier and amine catalysts have been shown to influence stability of silane-silica bonding in composites.

(4) A state-of-the-art report on radiopaque plastics in dentistry was prepared.

(5) A silver staining technique developed to assist investigation of mechanisms of degradation and wear in composite restorations yields useful information on subsurface microdefects in in vivo and in vitro worn specimens. In vitro wear with a pin-on-disc machine indicates increased wear of a composite is generated by going from a very hard (apatite) pin to a softer (stainless steel) pin. A wear test placing greater emphasis on shear forces generated via food particle interplay with teeth has been developed.

(6) With thermal expansion measurements, significant differences in the excess volume retained on cooling porcelains fired as per manufacturers' recommendations. Gap and shape changes in a porcelain veneered to alloy split ring offer promise for determining compatibility of porcelains for alloys.

SUMMARY

The research on dental materials that is described in this report is a part of a larger total effort that is carried out in collaboration with the American Dental Association Health Foundation. The U. S. Army and Navy Medical R&D Command and the School of Dentistry, Georgetown University are also part of this collaborative effort through support funding and/or assignment of research personnel.

While the bulk of the research progress in this report represents only the efforts of NBS staff supported under the Interagency Agreement with NIDR, there will of necessity be a degree of contribution that originates through the intentionally strong interaction among all persons participating in this collaborative dental program.

The objective is to effect improved dental health through development of new knowledge and better understanding of the mechanical, chemical, and physical properties of restorative and caries-preventive materials and the mechanisms by which clinical performance is governed.

A wide variety of techniques has been brought to bear to generate approaches to new and improved adhesive restorative dental materials These include: syntheses of components to improve current composite restorative materials and pit and fissure sealants and development of techniques that can be used to examine the extent of the polymerization reaction in dental resins and components, investigation of new approaches to bonding restorations to tooth surfaces, determination of the mechanisms by which composite systems wear and degrade in clinical use coupled with production of accelerated laboratory wear test data, and development of characterization methods and data for analyzing the compatibility of dental porcelains for base metal alloys.

A wide range of analytical techniques have been explored for utility in the investigation of the state, e.g. reacted or unreacted, of the carbon-carbon double bonds characteristic of the methacrylate monomers that are polymerized in the hardening reaction of dental resins and composites. Complete reaction of this double bond in a dimethacrylate produces chain lengthening as well as cross linking - both characteristics which influence mechanical properties and probably wear resistance. Unreacted double bonds incorporate potential oxidative degradation sites and if they are present in the hardened composite as a component in a monomethacrylate, a plasticizing effect can occur and the potential for extraction by oral fluids exists. The advantages and disadvantages of Fourier transform infrared (FTIR), Raman and ^{13}C NMR spectroscopy as well as differential scanning calorimetry are being assessed, and initial data have been obtained with the analytical techniques that are most appropriate to the problem.

Evaluation of several previously synthesized amines as polymerization accelerators for dental resins and composites has been completed with the result that one amine, 4,4,N-diethylaminophenylacetic acid, is sufficiently reactive to be used at a concentration one fourth to one fifth that of currently employed amines. This very low amine concentration coupled with its anticipated generic biocompatibility offers much promise for its use with dental composite systems. On the other hand, these more reactive amines when combined with very heat stable peroxyester initiators unfortunately did not produce composite formulations with significantly improved storage stability.

An important factor in the durability of dental composite restorations is the effectiveness of the coupling between reinforcing filler and the resin matrix. Experimentation on the effect of the nature of the carrier solvent used to deposit a silane coupling agent on the filler particles has now shown that certain solvent types in conjunction with selected amines resulted in greater reaction of the coupling agent and a consequently improved hydrolytic stability in the silica-silane bond.

A state-of-the-art report on the use of radiopaque plastics in dentistry was prepared for review by the American Dental Association Council on Dental Materials, Instruments and Equipment. The frequency of incidents such as ingestion, inhalation, or embedding plastic materials or devices has been shown to be low but the severity of such incidents demands rapid location, diagnosis and removal. Most foreign body accidents are found to involve partial or full plastic dentures but a case for radiopaque materials can also be made for composite filling materials, temporary crown and bridge materials and impression materials. Applicable radiopaque standards will be a requirement.

Synthesis of several 2-ethoxyphenol (guaiacol) derivatives, investigation of their reaction with metal oxides and evaluation of the properties of the resulting cements indicated cements with properties intermediate to those of zinc oxide eugenol and ethoxybenzoic acid can be readily formulated.

PolySAM-1, a multifunctional surface-active amine polymerization accelerator and several simpler surface-active amine promoters were evaluated as polymerization accelerators and adhesion promoters. While strength measurements on BIS-GMA composites formulated with hydroxyapatite as filler did not yield adhesion results as definitive as those obtained by applying a similar analysis to silanized and unsilanized glass filler composites, the indication is that certain surface-active amine promoters under selected conditions enhance bonding of dental resins to hydroxyapatite.

Understanding the mechanism of degradation and wear in dental composite is a crucial first step to developing more durable materials. To this end a silver staining technique has been demonstrated to yield useful information regarding the presence or absence of subsurface microdefects in both in vivo and in vitro worn specimens. Examination of a limited number of removed class 2 restorations that showed anatomical form loss revealed zones of damage 10-200 μm beneath the external surface. As a result of preliminary silver staining results, an in vitro wear test was developed to place greater emphasis on shear forces via viscous media that simulate those of three party (opposing teeth and food particles) interplay in the mouth. Replica microscopy and the silver staining techniques are to be used to determine wear damage in this accelerated in vitro test. A parallel project involves efforts to ascertain the extent of interaction of solutions of known solubility parameter with BIS-GMA resin. Microhardness measurements and silver staining indicate negligible interaction with organic acids or water but strong interaction with certain organic solvents. These effects are to be correlated with in vitro wear results.

Using a pin-on-disc accelerated wear test where the volume of restorative material in the disc that is lost per unit time or distance is the measure of the wear rate of a pin-on-disc couple, the wear rate of a composite has been shown to be much increased by going from a very hard (tooth enamel or synthetic apatite) to a softer (stainless steel) pin. By contrast, the wear rate of dental amalgams is little affected by choice of pin. In pin-on-disc wear measurements involving amalgam, the presence of a passive layer on the amalgam similar to that presumed to be present constantly in the clinical situation, has been shown to significantly retard wear.

In the area of dental alloy and ceramic research, thermal expansion measurements on a number of porcelains and alloys have been completed, a preliminary report presented at the 1980 IADR meeting and an invited paper given at the 1980 Annual Meeting of the International Precious Metals Institute. Significant differences in the porcelains, fired according to manufacturers instructions, have been observed in that large variations in the amount of excess volume retained upon cooling is indicated. Since compatibility of porcelain for alloy (emphasis is on base metal alloys) depends not only on stresses set by differences in thermal contraction but on geometrical shape and the thermal relief of stress, a split ring constructed from porcelain veneered to the alloy and approximately equal in size to a dental crown has been designed. Experimental and theoretical results of studies of gap and shape changes with the split ring indicate that a previously derived mathematical expression for compatibility is not adequate to describe the complex interactions and that some form of stress relief occurs at temperatures lower than the glass transition temperature, T_g, of the porcelain. A modification of the sprue system used in an earlier version of a castability test developed in this laboratory has reduced specimen to specimen variation with base metal alloys by more than one-half. Preliminary visual examination of cast clinical crowns indicated a direct correlation between castability test scores and the quality of the margins of clinical crowns cast from the same materials.

In an effort to define isotopes that may present hazards upon neutron activation following sublethal neutron exposure, calculations have been made to estimate the additional dose of radiation (β and γ) delivered to local oral tissue by neutron activated gold crowns. The calculations indicate a 50 REM neutron dose could subsequently be accompanied by as much as 30 REM.

INTRODUCTION

The National Bureau of Standards is primarily a measurement organization. Paths from measurement to improved dental service lead from measurement and characterization to development of new techniques for using materials, to laboratory prototypes of improved materials and devices, to clinical evaluation, and finally, to commercial production by industry.

The dental research program at NBS is a cooperative effort both in personnel and funding, involving the American Dental Association and the U. S. Army and Navy Medical R&D Commands. With the exception of the research on porcelain fused to base metal alloy - research also participated in and partially funded by the U. S. Navy Medical R&D - the research described herein is only that portion of the dental program supported by interagency agreement with the National Institute of dental Research.

The objective of the research effort discussed briefly in the following pages is to effect improved dental health through development of new knowledge and better understanding of the mechanical, chemical and physical properties of materials used or potentially of use in restorative and preventive dental practices. The four major areas of research as approved in the interagency agreement are given below:

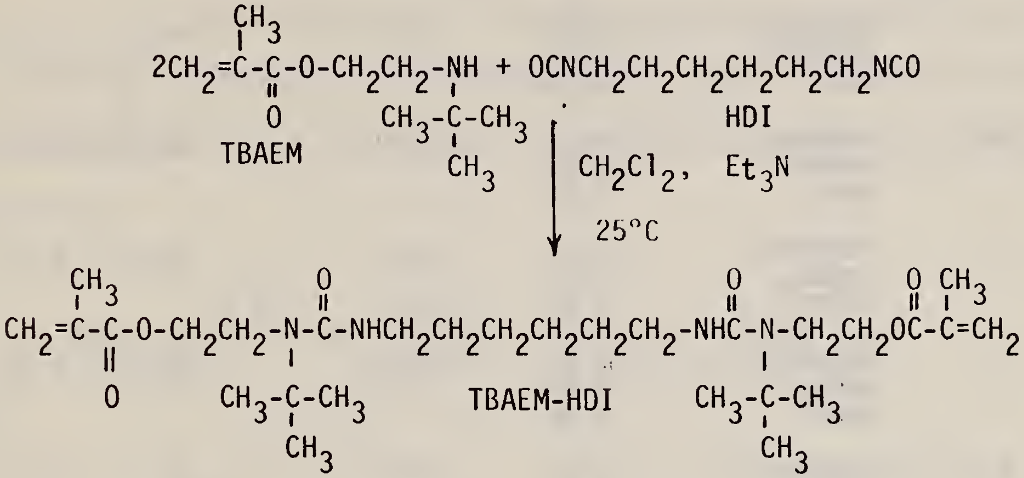
I. Dental Composite, Resin, Sealant and Cement Chemistry and Development
II. Development of Adhesive Bonding Techniques
III. Wear Resistance and Mechanical Properties of Dental Materials
IV. Dental Alloys, Ceramics and Implants

I. Dental Composite, Resin, Sealant, and Cement Chemistry and Development

A. New Monomers for Reducing Polymerization Shrinkage

1. Diurea Dimethacrylate Monomer

The synthesis of the diurea dimethacrylate, TBAEM-HDI, from the reaction of N-_t_-butyl-2-aminoethyl methacrylate (TBAEM) and hexamethylene diisocyanate (HDI) was described earlier [1].



$$2CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2CH_2{-}NH{-}C(CH_3)_3 + OCNCH_2CH_2CH_2CH_2CH_2CH_2NCO \xrightarrow[25^\circ C]{CH_2Cl_2,\ Et_3N}$$

$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2CH_2{-}N(C(CH_3)_3){-}C({=}O){-}NHCH_2CH_2CH_2CH_2CH_2CH_2{-}NHC({=}O){-}N(C(CH_3)_3){-}CH_2CH_2OC({=}O){-}C(CH_3){=}CH_2$$

TBAEM

HDI

TBAEM-HDI

Preliminary structural confirmation of the white waxy solid monomer was obtained by infrared and NMR spectral analyses. TBAEM-HDI has a molecular weight of 538 compared to 512 for BIS-GMA and has two tri-substituted urea groups, each having a bulky t-butyl substituent. The relatively high molecular weight and hindered nature of the urea linkages in this monomer should yield dental resin formulations with low polymerization shrinkage. Setting time and tensile strength values for a few formulations are given in Table 1.

The diametral tensile strengths of the composites, all of which exhibited excellent initial color and very good color stability, were above the ADA specification minimum (34 MPa). These formulations

Table 1

SETTING TIMES AND 24-HR. DIAMETRAL TENSILE STRENGTHS OF EXPERIMENTAL COMPOSITES* BASED ON TBAEM-HDI

Formulation	Monomer System	Wt. %	Setting Time (Min.)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of Specimens)
1	TBAEM-HDI NPGDMA DHPPT[a]	77.0% 22.7% 0.27%	3.0	43.7 ± 2.5 (5)
2	TBAEM-HDI NPGDMA[b] DHPPT	77.0% 22.6% 0.37%	2.5	42.6 ± 3.1 (4)
3**	TBAEM-HDI HMGDMA[c] DHPPT	75.0% 24.7% 0.3%	2.0	39.6 ± 3.0 (5)
4	TBAEM-HDI HMGDMA DHPPT	75.0% 24.7 0.3%	2.0	44.6 ± 3.9 (4)
5	TBAEM-HDI DMGDMA[d] DHPPT	85.0% 14.7% 0.3%	2.5	45.2 ± 3.5 (5)
6	TBAEM-HDI TEGDMA DMSX[e]	82.0% 17.9% 0.13%	3.5	37.6 ± 2.2 (5)
7***	Same as above		3.0	40.5 ± 1.4 (5)
8	TBAEM-HDI TEGDMA[f] DMSX	70.0% 29.8% 0.23%	1.5	44.8 ± 1.4 (5)
9	TBAEM-HDI TEGDMA DHPPT	80.0% 19.7% 0.3%	2.0	42.2 ± 3.4 (5)
10	TBAEM-HDI TEGDMA DHPPT	80.0% 19.6% 0.4%	1.5	46.4 ± 1.5 (5)

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*Powder/liquid formulations used with P/L = 3 except where noted. Powder is usual glass filler silanized and coated with 1% Benzoyl Peroxide (BP).

**P/L = 2.5.

***P/L = 2.5 and blended glass filler used (equal parts 1% BP and 0.3% AA glass).

[a] DHPPT = N,N-di-(2-hydroxypropyl)-p-toluidine.

[b] NPGDMA = Neopentylglycol dimethacrylate.

[c] HMGDMA = Hexamethyleneglycol dimethacrylate.

[d] DMGDMA = Decamethyleneglycol dimethacrylate.

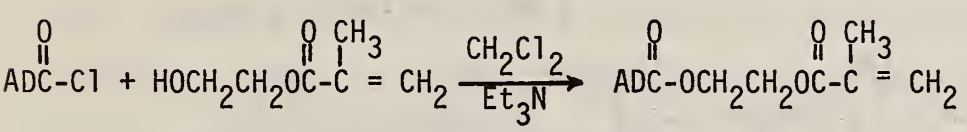
[e] DMSX = N,N-dimethyl-sym-xylidene.

[f] TEGDMA = Triethyleneglycol dimethacrylate.

employed diluent monomers that are commonly used with BIS-GMA dental resin systems. Assuming a comparable degree of polymerization for TBAEM-HDI and BIS-GMA monomer systems, the somewhat lower DTS values found in the case of the former may be indicative of a less brittle organic matrix.

2. Methacryloxyethyl-1-Adamantane Carboxylate

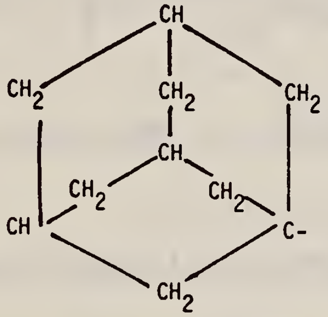
The synthesis of the bulky monofunctional monomer, methacryloxyethyl-1-adamantane carboxylate (MAC), from 1-adamantane carboxyl chloride ($\mathrm{AD\overset{O}{C}\text{-}Cl}$) and 2-hydroxyethyl methacrylate (HEMA) was described earlier [1].



$$\mathrm{AD\overset{O}{\overset{\|}{C}}\text{-}Cl + HOCH_2CH_2O\overset{O}{\overset{\|}{C}}\text{-}\overset{CH_3}{\overset{|}{C}} = CH_2 \xrightarrow[Et_3N]{CH_2Cl_2} AD\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2O\overset{O}{\overset{\|}{C}}\text{-}\overset{CH_3}{\overset{|}{C}} = CH_2}$$

where

AD =



$\mathrm{Et_3N}$ = triethylamine

A preliminary dental resin formulation employing this non-volatile liquid monomethacrylate of relatively low viscosity, with silanized, peroxidized glass filler gave encouraging results.

Experimental Formulations		P/L	Setting Time (min)	Diametral Tensile Strength
BIS-GMA	64.8%	3	3.0	45.2 1.4 (4)
MAC	26.4%			
CDMDMA[a]	8.6%			
DMAPE[b]	0.2%			

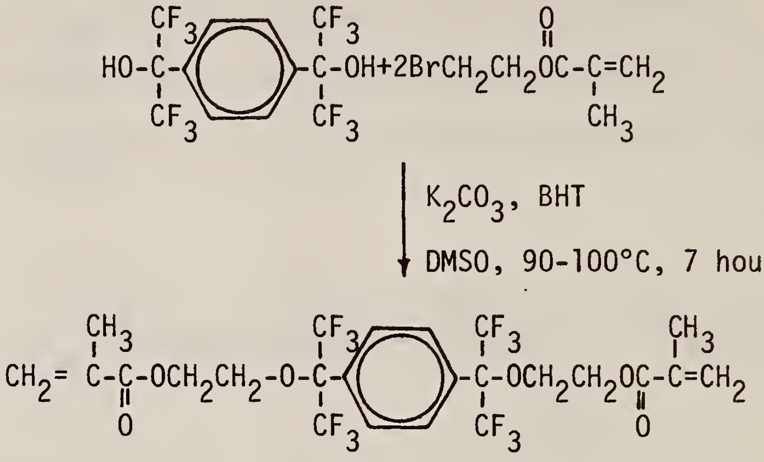
The composite exhibited excellent initial color

a = Cyclohexane dimethanol dimethacrylate

b = 4-N,N-dimethylaminophenethanol

3. Bis-p-(2-Methacryloxyethoxyhexafluoro-2-Propyl) Benzene

The previously described [1] method used in the synthesis of the dimethacryloxyethoxy derivative of meta bis(2-hydroxyhexafluoro-2- propyl) benzene was applied to the synthesis of the corresponding para isomer as shown below.



K_2CO_3, BHT

DMSO, 90-100°C, 7 hours

Bis-p-MEHFPB (MW = 634, m.p. 112-115)

Preliminary confirmation of the structure of this solid monomer was obtained by IR analysis.

B. Development of New Initiator/Accelerator Systems

1. Amine Accelerators

Amines are crucially important to the hardening of dental resins since in situ polymerization requires chemical means rather than thermal to generate free radicals from the peroxide initiator. Since amines can be a source of discoloration, of toxic response and can through the manner in which they influence the rate of free radical formation affect the molecular weight and molecular weight distribution of the polymeric matrix, it is very important to develop information that can yield efficient, biocompatible and non-color inducing amines.

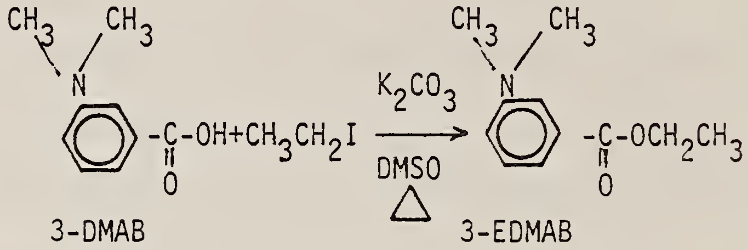
a. Stucture-Property Studies Employing Slower Acting Amine Types Including Surface Active or Adhesive-Generating Amines

The critical properties (e.g. reactivity, color stability, biocompatibility, etc.) of tertiary aromatic amine polymerization accelerators are governed by aromatic ring substituents as well as substituents on the amine nitrogen. We have studied the effects of such substituents by examining setting times (Gilmore needle test) and diametral tensile strengths (DTS) of composites prepared from experimental powder/liquid (P/L) formulations consisting of silanized glass filler coated with 1% BP and the liquid resin system BIS-GMA (7)/ TEGDMA (3), containing the amine accelerator.

From the structure-property considerations, the commercially available tertiary aromatic amines, 4-N,N-dimethylaminobenzoic acid (4-DMAB) and its ethyl ester (4-EDMAB) would be expected to be slow-acting accelerators and have enhanced oxidative and color stability due to the electron withdrawal character of their respective para substituents. Both 4-DMAB and 4-EDMAB, by analogy with their respective parent compounds, 4-aminobenzoic acid (a Vitamin B, anticanitic and sunscreen agent) and ethyl-4-aminobenzoate (the local anesthetic, Benzocaine), should have excellent biocompatibilities.

With relatively slow-polymerizing monomers such as methyl methacrylate, the polymerization proceeds much slower by many hours both with 4-DMAB and 4-EDMAB than with a fast-acting amine accelerator such as N,N-dimethyl-p-toluidine (DMPT). However with relatively fast polymerizing monomer systems, such as BIS-GMA (7)/TEGDMA (3), clinically acceptable setting times are obtainable with these slow-acting amine accelerators (Tables 2 and 3), using the usual powder/liquid formulation technique. In addition, the mechanical properties of these composites, as evidenced by their DTS values, are also quite acceptable (minimum DTS = 34 MPa), comparable to those obtained with the usual fast-acting amine accelerators. A manuscript entitled "Slow-Acting Amine Polymerization Accelerators. I. Para-Dimethylaminobenzoic Acid and its Ethyl Ester" has been accepted for publication in the Journal of Dental Research.

A parallel study of the accelerative behavior of the corresponding meta isomeric amines, 3-N,N-dimethylaminobenzoic acid (3-DMAB) and its ethyl ester (3-EDMAB) was initiated. The commerically unavailable 3-EDMAB was synthesized from 3-DMAB by the method indicated.



The product, a pale yellow liquid, was at least 98% pure by gas-liquid chromatographic analysis. Preliminary structural confirmation was obtained by infrared analysis. The setting times and diametral tensile strengths of composites prepared with 3-DMAB and 3-EDMAB over a wide concentration range are summarized in Tables 4 and 5.

The initial appearances of composites prepared with 3-DMAB and 3-EDMAB were excellent. On storage in the dark at 37°C in a 100% relative humidity bath, the 3-EDMAB composites retained their

Table 2

Effect of 4-DMAB Concentration on the Setting Time and Diametral Tensile Strength of an Experimental Composite* With No Added BHT

4-DMAB Concentration Wt%	4-DMAB Concentration mMolal	Setting Time (min)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of specimens)
0.10	6.0	9.0	44.7 ± 2.6 (5)
0.165	10.0	6.0	46.9 ± 3.0 (5)
0.20	12.1	6.5	48.8 ± 2.5 (5)
0.25	15.2	5.0	50.5 ± 2.0 (9)
0.28	17.0	5.0	48.0 ± 1.5 (6)
0.30	18.2	5.0	47.9 ± 5.3 (11)
0.33	20.0	5.5	50.8 ± 1.6 (4)
0.40	24.2	5.5	49.9 ± 3.5 (12)
0.45	27.3	4.0	51.4 ± 2.9 (11)

*Powder/liquid formulations employing powder/liquid ratio of 3. Powder is silanized glass filler and coated with 1% BP. Liquids are monomer mixtures consisting of 7 parts BIS-GMA and 3 parts TEGDMA containing the indicated concentrations of 4-DMAB but no added BHT.

Table 3

Effect of 4-EDMAB Concentration on the Setting Time and Diametral Tensile Strength of an Experimental Composite Material* With No Added BHT

4-EDMAB Concentration Wt%	mMolal	Setting Time (min)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of specimens)
0.20	10.4	11.0	44.3 ± 1.6 (5)
0.26	13.5	8.0	50.6 ± 1.0 (3)
0.30	15.6	8.0	51.2 ± 2.2 (5)
0.40	20.7	7.5	47.7 ± 2.6 (7)
0.50	25.9	6.0	54.2 ± 1.1 (3)
0.60	31.1	5.5	50.9 ± 1.4 (4)
0.70	36.3	5.5	54.9 ± 1.5 (4)
0.80	41.4	5.5	51.7 ± 1.9 (5)
0.90	46.6	5.0	52.0 ± 1.5 (4)
1.00	51.8	4.5	46.3 ± 3.1 (12)
1.10	57.0	4.0	49.9 ± 2.4 (6)
1.30	67.4	4.5	53.8 ± 2.3 (7)

* Same as in Table 1 except for 4-EDMAB

Table 4

Effect of 3-DMAB Concentration on the Setting Time And Diametral Tensile Strength of an Experimental Composite*

With No Added BHT

3-DMAB Concentration Wt.%	mMolal	Setting Time (Min.)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of Specimens)
0.12	7.3	4.5	43.1 ± 1.2 (7)
0.165	10.0	3.5	48.5 ± 1.9 (5)
0.20	12.1	3.0	50.2 ± 2.5 (6)
0.25	15.2	2.5	51.5 ± 3.8 (6)
0.28	17.0	2.5	49.0 ± 4.2 (8)
0.33	20.0	2.0	52.9 ± 2.6 (4)
0.40	24.2	2.5	49.4 ± 2.6 (8)
0.50	30.3	2.0	56.8 ± 4.9 (4)
0.60	36.4	2.0	50.6 ± 4.2 (12)
0.70	42.4	1.5	56.3 ± 4.0 (5)

* Same as in Table 2 except for 3-DMAB

Table 5

Effect of 3-EDMAB Concentration on the Setting Time and Diametral Tensile Strength of an Experimental Composite* with no Added BHT

3-EDMAB Concentration Wt%	3-EDMAB Concentration mMolal	Setting Time (min)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of specimens)
0.10	5.2	6.0	46.1 ± 3.3 (8)
0.20	10.4	5.0	48.9 ± 3.2 (11)
0.25	13.0	4.0	52.2 ± 2.4 (6)
0.30	15.6	3.25	52.1 ± 1.9 (6)
0.40	20.7	3.75	48.2 ± 3.8 (6)
0.50	25.9	3.5	51.3 ± 3.4 (7)
0.60	31.1	3.0	53.1 ± 2.0 (7)
0.70	36.3	3.0	51.1 ± 2.6 (6)
0.80	41.4	2.75	53.8 ± 2.9 (5)
0.90	46.6	2.5	52.4 ± 3.0 (6)
1.0	51.8	2.75	52.6 ± 2.9 (6)
1.4	72.5	2.0	51.6 ± 3.8 (10)
2.0	103.6	2.0	51.8 ± 2.8 (5)

* Same as in Table 2 except for 3-EDMAB

initial appearance almost as well as those prepared with 4-EDMAB which is excellent from this standpoint.

Although classified as slow-acting amine accelerators, an examination of the setting time data of Tables 2-5 reveals significant differences in reactivity between 4-DMAB, 4-EDMAB, 3-DMAB and 3-EDMAB. Of these less reactive polymerization accelerators, 4-EDMAB is the slowest promotor while the most reactive is 3-DMAB. The order of decreasing accelerative reactivity appears to be 3-DMAB > 3-EDMAB > 4-DMAB > 4-EDMAB. This is in accord with the relative electron-withdrawing character of the aryl substituents $-CO_2H$ and $-CO_2C_2H_5$ and their ring position; that is, the reactivity data correlate well with the accepted $\sigma+$ values. Within experimental error, average diametral strengths of composites prepared using these amines were not significantly different, although the fastest of these accelerators, 3-DMAB, did give some of the highest individual DTS values (∿60 MPa).

These relatively less reactive accelerators may have several advantages over the commonly used fast-acting accelerators:

1) there is less need for the use of inhibitors or retarders to control working and setting times,

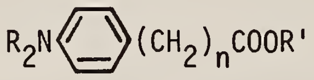
2) they permit a wide amine concentration range to be studied with dental resin systems which are usually fast polymerizing in nature. This may prove helpful in obtaining a better understanding of the acyl peroxide/amine initiator system and may permit the determination of the extent of polymerization occuring in thermosetting monomers by such techniques as differential scanning calorimetry.

3) The use of surface-active accelerators such as 4-DMAB and 3-DMAB may improve the adhesiveness of dental restorative and sealant materials to apatitic tissue.

4) The relatively superior retention of the excellent initial appearance on storage at 37°C in the dark of composites prepared with 4-EDMAB and 3-EDMAB compared to the similar composites prepared with fast-acting amine accelerators may have implications for improving the esthetics of these dental materials by the use of less electron-rich accelerators.

b. Development of Fast-Acting, Biocompatible Amine Accelerators

This research was undertaken to synthesize color stable amines which are more reactive accelerators than those commercially available, and to evaluate those accelerators which can be expected to be more biocompatible and less toxic than tertiary amines presently used. This year (1) the synthesis and characterization of structurally related homologues and derivatives of 4-N,N-dimethylaminophenylacetic acid (DMAPAA) I, and N,N-dialkylaminophenethanol, II, was completed.



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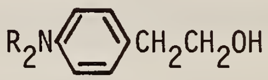


II

(2) Correlation of the structure of resulting acids, esters and alcohols of varying chain length and N-alkyl substitution (where R = CH_3,C_2H_5; R' = H,CH_3,C_2H_5 and n = 1 or 2) with their reactivity in the peroxide-initiated polymerization of composites was determined, and (3) presently used accelerators were compared with these compounds with regard to their effect on such properties of the cured composite as mechanical strength, color stability and water sorption.

Infrared, NMR, gas chromatographic and elemental analysis were used to establish the structure and purity of previously synthesized 4-N,N-diethylaminophenethanol, 4-N,N-diethylaminophenylacetic acid-ethyl ester and 4-N,N-dimethylaminophenylpropionic acid.

A number of unsuccessful attempts were made to synthesize 4-N,N-diethylaminophenylacetic acid (DEAPAA) by basic hydrolysis of the ethyl ester. Acid hydrolysis of this compound yielded the desired product.

During this reporting period the evaluation of the amines previously synthesized [1,2] as accelerators in the benzoyl peroxide initiated cure of dental composite formulations was completed. The 4-N,N-diethylaminophenylacetic acid (DEAPAA) was found to be the most reactive amine ever prepared. As can be seen from Table 6, concentrations as low as 3 mmolal of this accelerator (compared to 15 mmolal concentration for the commonly used dimethyl-p-toluidine, DMPT) in the monomeric liquid of standard formulations yield a cure in 4.5 min. Without BHT inhibitor this curing time is reduced to 1.5 min, a time which is too short for clinical practice. Too rapid a polymerization can be avoided by increasing the BHT inhibitor concentration in the liquid to 0.3 or 0.4%, which decreases the strength of the composite only slightly.

The mechanical characteristics of composites containing the amines under study were highly satisfactory. Thus, the cured composites had physical properties equal or better than those obtained for commercial composites. For all formulations the tensile strength considerably exceeded the minimum requirement of 34 MPa of the Specification for Direct Filling Resins. Optimum properties (tensile

Table 6

Properties of Composites Cured With 4,-N,N-Diethylaminophenyl Acetic Acid as Accelerator

Powder: Corning Glass 7724, silanized and coated with 1% benzoyl peroxide

Liquid: 72.4% BIS-GMA, 27.6% 1,6-hexamethylene, glycol dimethacrylate and 0.2% BHT

Powder-liquid ratio: 3/1

mMolal Conc. in Liquid	Setting Time Min.	Tensile Strength, MPa	Compressive Strength, MPa	H_2O Sorption mg/cm^2
3	4.5	36(2)[f]	-	-
3[a]	1.5	49(3)	-	-
5	2.5	44(1)	245(7)[f]	0.56(.03)
7	2.5	45(1)	275(3)	-
7[b]	2.5	44(5)	-	-
9	2.0	46(4)	275(10)	-
11	2.0	46(4)	284(6)	-
13	2.0	49(4)	272(6)	-
15	1.5	52(3)	268(9)	-
17	1.5	54(4)	303(9)	0.58(.02)
17[c]	2	52(2)	280(6)	-
17[d]	2	50(3)	294(6)	-
17[b]	1.25-1.5	55(2)	-	0.57(.02)
19[e]	1.5	54(2)	292(15)	-
19	1.25-1.5	49(3)	-	-

For comparison identical composite formulations polymerized with 4,-N,N-dimethyl-p-toluidine (DMPT) have the following properties:

15	4.5	45.9(4)	276(22)	.60(.05)
17	3	43.0(3)	246(10)	.58(.00)
19	4.5	47.6(3)	246(17)	.56(.03)

---

[a] Prepared without inhibitor

[b] 0.4% ultraviolet absorber added

[c] Prepared with 0.3% BHT

[d] Prepared with 0.4% BHT

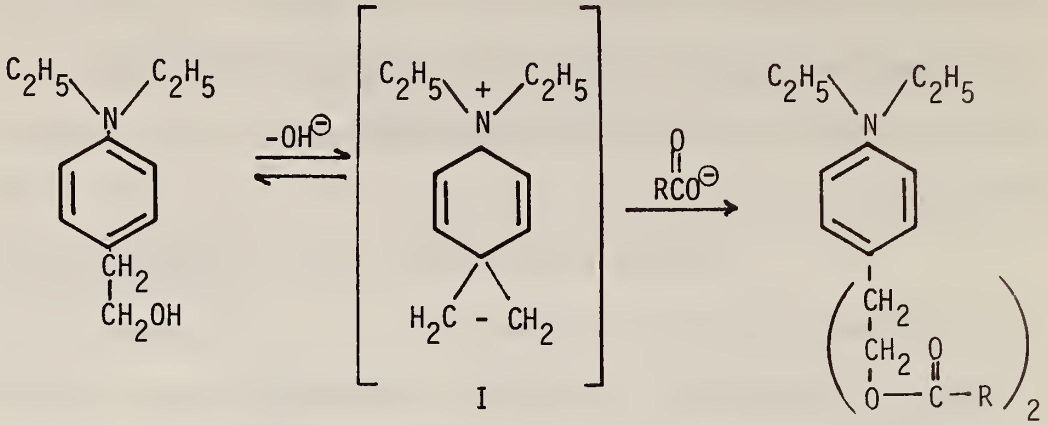
[e] Prepared with 0.25% BHT

[f] Values in parenthesis give standard deviation

strength 55 MPa, compressive strength 303 MPa) were found for formulations containing 17 mmole concentration of the accelerator. On lowering the BHT inhibitor concentrations in these formulations even higher mechanical strength values were obtained. Substituting 1,10-decamethylene glycol dimethactylate for the 1,6-hexamethylene homologue as diluent did not change the characteristics of the composite appreciably.

The much lower concentration of DEAPAA required to give an adequate cure for the composite (i. e., about one-half the concentration of accelerators such as DMPT) imparted a nearly colorless or very light shade to the resin which is much less than is obtained with commercial products. Incorporation of an ultraviolet stabilizer in 0.4% concentration did not change the physical properties of the composite. The cured specimens containing this stabilizer showed no visible change after being subjected to the color stability test of the ADA Specification No. 27.

4-N,N-dimethylaminophenylacetic acid is absorbed on hydroxyapatite and appears to improve bonding of reactive adhesive formulations to dentin. Thus an attempt has also been made to synthesize the diethylaminophenethanol monosuccinate. This compound should be a highly reactive accelerator containing free acid groups which may interact with dentin. Equimolar concentrations of dimethylaminophenethanol and succinic anhydride were heated to 68°C for 1 1/2 hours. After separation of the reaction mixture and recrystallization from ethanol-water a tan-colored solid MP 85-86°C was obtained which proved a rapid accelerator for the polymerization of composites. ^{13}C NMR analysis indicates, however, that this compound is the diester probably formed through the stabilized intermediate (I).



Further efforts will be made to synthesize the monosuccinate by employing even milder reaction conditions.

c. Amines as Photoinitiators of Polymerization

The 4-N,N-dimethyl- and 4-N,N-diethylaminocinnamic acids previously synthesized act as photo-initiators for the polymerization of resins in sunlight or under UV radiation. To evaluate their possible usefulness as initiators for resins cured by visible light, typical BIS-GMA formulations containing these compounds were prepared. However, the low solubility of the cinnamic acids in BIS-GMA and diluent allowed too little amine (< 0.2%) to be incorporated for effective polymerization under a sunlamp.

To obtain a more soluble initiator the ethyl ester of diethylaminocinnamic acid (DEACA-EE) was synthesized. Monoethylmalonate was prepared by hydrolysis of diethylmalonate according to Breslow [3]. The DEACA-EE was prepared from p-diethylaminobenzaldehyde and the monoethylmalonate by the procedure of Bolat [4]. The product melted at 47-48.5°C and had a λ_{max} at 372-374 μm. A very yellow one-percent solution of the product in BIS-GMA and diluent retained its prohibitive color on being cured by sun lamp irradiation for three minutes. Although the shade of the resin was improved by reducing the photoinitiator concentration, the time to cure was increased excessively and this photoinitiator does not offer promise for dental application.

d. Amines for Improved Color of Denture Base on Repair Resins

For some clinical applications of denture base or repair resins colorless or nearly colorless shades are required. A study was initiated to determine the suitability of the dialkylaminoacetic acids or phenethanols previously synthesized in this laboratory as accelerators for room temperature-curing denture resins. Mixes using commercial powder without or with benzoyl peroxide (3%) and different concentrations of the tertiary amines in methyl methacrylate had adequate working times. The cured resin showed no trace of discoloration when dimethylaminophenethanol (DMAPE) was used as accelerator and exposure to a sun lamp produced only a light yellow shade. On addition of 0.4% Tinuvin P (an ultraviolet stabilizer) to the formulation the color stability of all specimens was improved greatly and only a very slight, hardly perceptible, discoloration of the irradiated specimen containing 0.5% DMAPE was observed. The shade and color stability of the DMAPE containing materials appeared slightly better than those polymerized with N,N-dimethyl-p-tert-butylaniline which previously was considered the least color-producing accelerator.

Measurements to compare the physical properties of resins containing these accelerators are being made. Water sorption of materials employing the various amines ranged from 0.4 to 0.8 mg/cm^2 which is within the requirements of the ADA Specification No.12 for Denture Base Resins.

2. Non-Amine Accelerators

a. Ascorbic Acid Systems

Previously [2] we had shown that minute amounts of copper compounds either dissolved in the monomer system from the start or added in an apparently insoluble form (copper mordanted hydroxyapatite powder) could significantly decrease the cure time of peroxide-ascorbic acid type initiator systems. Using an experimental glass containing minute amounts of copper salts, we have preliminary evidence that copper even in this state can have catalytic properties on the free radical initiation reaction provided an ascorbic type reducing agent is employed. No additional acceleration is noted in the setting time unless ascorbic acid or palmitate is part of the initiator system along with the copper containing glass. Table 7 compares the effect of this catalytic glass on the setting time of several composite formulations. The composites exhibited no visible coloration and had excellent color stability. Analogous results were obtained with a cumene hydroperoxide-ascorbic acid type initiator system.

The copper containing glass was then silanized with 3-methacryloxypropyltrimethoxysilane using the cyclohexane propylamine method described elsewhere in this report (Section I.D.). In Table 8 are given the results showing the effect of this silanized copper glass on the setting time and the DTS values of composites using only t-butylperoxymaleic acid as the initiator. Blending 10% of silanized copper-containing glass with copper-free silanized glass coated with 1% T-BPM

TABLE 7

COMPARATIVE SETTING TIMES[a] OF EXPERIMENTAL COMPOSITES[b] USING ASCORBIC ACID TYPE INITIATOR SYSTEMS WITH AND WITHOUT CATALYTIC GLASS

Formulation	Liquid Monomer	Powder	P/L	Setting Time (Min.)
1	BIS-GMA(7) TEGDMA(3) 0.06% Tyrosine 1.0% BP 1.3% TBPM[c]	0.3% AP[d] on silanized glass	3	7.0
2	Same as ①	0.3% AP[d] on silanized glass + 11% Cu glass	3	4.0
3	BIS-GMA(7) TEGDMA(3) 0.06% Tyrosine 1.0% BP 1.6% TBPB[e]	0.3% AP[d] on silanized glass	3	4.0
4	Same as ③	Same as ②	3	2.5
5	Same as ①	Only Cu glass	3	No Set
6	Same as ③	Same as ⑤	3	No Set

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[a] Gilmore needle test at 37°C.

[b] Powder/liquid formulations used throughout.

[c] TBPM = t-butylperoxymaleic acid.

[d] AP = Ascorbyl palmitate.

[e] TBPB = t-butylperbenzoate.

Table 8

Effect of Silanized Copper Glass on Setting Time and Diametral Tensile Strength of Two Experimental Composites

Formulation	Liquid	Powder	Setting Time (min.)	DTS ± Std Dev (MPa) (No. of Specimens)
A	BIS-GMA (7) TEGDMA (3) 0.6% AP	1% TBPM silanized glass	7.0	43.0 ± 2.1 (6)
B	Same as A	90% 1% TMPM silanized glass + 10% silanized Cu Glass	3.5	44.4 ± 2.3 (6)
C	UDM 0.5% AP	Same as A	8.0	44.2 ± 1.5 (5)
D	Same as C	Same as B	5.5	48.5 ± 3.0 (4)

AP = Ascorbyl Palmitate
TBPM = T-butylperoxymaleic acid
UDM = urethane dimethacrylate (Vivadent)
All composites prepared using powder/liquid ratio of 3

halved the setting time obtained with similar formulations using the same silanized peroxidized glass filler but without the copper glass. The effect of this catalytic glass on the diametral tensile strength of composites was less pronounced, although formulation D did show approximately a 10% increase over that of C (without Cu glass). All the composite specimens exhibited excellent initial color and color stability (no change on exposure to ultraviolet irradiation for 24 hours and no change on storage at 37°C in 100% constant humidity chamber for 2 weeks).

C. Analysis for Degree of Polymerization of Dental Resins

Infrared spectroscopy has been employed by several workers to examine the extent of polymerization of dental monomers. In the case of dental composite materials especially this technique can be hampered by the difficulties of sample preparation and by a strong interference in the critical vinyl absorption region by the siliceous filler component. We have initiated an investigation into alternate analytical techniques which may alleviate some of these problems. These techniques are: (1) differential scanning calorimetry (DSC), (2) ^{13}C solid state NMR spectroscopy and (3) laser Raman spectroscopy. In addition, we are conducting the traditional infrared spectroscopic comparative analyses of uncured vs cured dental resin systems by means of a recently acquired Fourier transform infrared (FTIR) instrument.

1. Differential Scanning Calorimetry (DSC)

DSC has been used to assess the extent of polymerization of both monofunctional and multifunctional vinyl monomers. The technique measures the thermal change, i.e. heat of polymerization, that accompanies the conversion of vinyl groups to saturate carbon to carbon bonds by self addition. The area under the recorded exothermic peak is proportional to the heat of polymerization and therefore, to the number of such vinyl groups reacted.

In this preliminary study DSC was used to ascertain the degree of polymerization or conversion, C, of an experimental monomer system consisting of 7 parts by weight of BIS-GMA and 3 parts by weight of triethylene glycol dimethacrylate (TEGDMA). The molar heat of polymerization (ΔHp) of lauryl methacrylate as determined by DSC (13.6 Kcal/mole) was used as the basis for calculating the conversion of vinyl groups to polymer. Thermally activated polymerizations of BIS-GMA (7)/ TEGDMA (3) were conducted using benzoyl peroxide as the initiator. Both the concentration of BP and heating rate employed in the DSC experiment affected the extent of polymerization as shown in Table 9 below:

Table 9. DSC Examination of BIS-GMA(7)/TEGDMA(3) Polymerization

BP Concentration	Heating Rate/Peak Exotherm	% Vinyl Reaction
0.4	2.5°C/min; 90°C	37
1.0	" "	51
2.2	" "	61
0.4	10°C/min; 110°C	73
1.0	" "	59

Several chemically activated polymerizations of the same monomer system yielded the results shown in Table 10.

Table 10. DSC Examination of Chemically Activated Polymerization of BIS-GMA (7)/ TEGDMA (3)

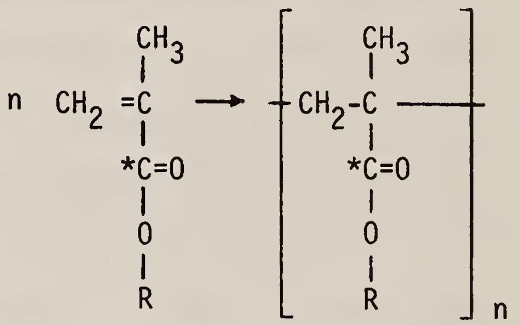
Accelerator, Conc. (wt %)	BP Conc. (wt %)	Peak Exotherm (°C)	% Vinyl Reaction
1) DMBA, 0.23	0.39	41	48
2) a) DHPPT, 0.42	1.0	57	56
b) " "	2.2	49	48
3) a) 4-DMAB, 0.5	1.0	58	46
b) 78% Glass paste	78% glass paste	82	61
4) 4-EDMAB, 1.3	2.2	52	53
5) AP, 0.56	1.0	40	51

From the above results it is evident that even at a high peak exotherm (e.g. paste/paste systems) approximately 40% of the vinyl groups have not reacted in the chemically activated system. Experimental difficulties are encountered when fast acting amine polymerization accelerators, such as p-t-butyl-N,N-dimethylaniline (DMBA) are employed. However, these fast promoters may be studied if the concentration of BP and amine are relatively low or if additional quantities of inhibitor are added to the monomer system. The use of a slower polymerizing monomer system would also permit their use in this type of DSC study. On the other hand, the slower-acting amine accelerators such as 4-dimethylaminobenzoic acid (4-DMAB) and its ethyl ester (4-EDMAB) as well as the relatively slow non-amine accelerator, ascorbyl palmitate, are well suited for this type of DSC experiment. The moderately fast amine promoter, N,N-bis(2-hydroxypropyl)-p-toluidine (DHPPT) is also amenable to this type of study.

The low melting solid analog of BIS-GMA, BIS-EDMA (the dimethacryloxyethoxy derivative of bisphenol A) with 1% BP had only about 40% conversion of vinyl groups on thermal polymerization (peak exotherm = 72°C), this result supports the expected relatively immobile nature of many pendant vinyl groups in the initial network polymer resulting from the polymerization of a rather inflexible difunctional monomer. BIS-GMA would be expected to yield similar results. An obvious potential application of the DSC method would be to evaluate diluent monomers that can maximize the conversion of these vinyl groups. In addition, DSC should be useful in studying the efficacy of different initiator systems and inhibitors.

2. Solid State ^{13}C NMR Spectroscopy

This technique is based on the change in the chemical shift of the carbonyl carbon of methacrylate monomers on their conversion to polymer.



$$n\ CH_2{=}\underset{\underset{\underset{R}{|}}{\overset{|}{O}}}{\underset{|}{\overset{*}{C}{=}O}}{\overset{CH_3}{\overset{|}{C}}} \longrightarrow \left[\, CH_2{-}\underset{\underset{\underset{R}{|}}{\overset{|}{O}}}{\underset{|}{\overset{*}{C}{=}O}}{\overset{CH_3}{\overset{|}{C}}} \,\right]_n$$

An example of the potential of this method is shown below for thermally and photochemically polymerized BIS-GMA. Quantitative analysis appears feasible and the presence of inorganic filler as occurs in the composite should only have a diluting effect which can be dealt with. (See Fig. 1)

3. Laser Raman Spectroscopy

The intense vinyl absorption plus a much less intense carboxyl absorption compared to that characteristic of IR spectroscopy offer potential advantages in terms of sensitivity for the analytical determination of degree of polymerization of dental resins. Also, sample geometry is less restrictive in laser Raman spectroscopy than it is in transmission IR spectroscopy.

4. Fourier Transform Infrared Spectroscopy

As compared to previously available IR instrumentation, the recently acquired FTIR instrument (Nicolet Model 7199) offers the potential for optimizing the sensitivity of IR spectroscopic analysis and thus to yield more quantitative data on the percent conversion of vinyl groups. Vinyl absorption is distinctive and uncomplicated by the usually overwhelming absorption due to the filler content of a composite.

D. Resin/Filler Coupling Improvement for Composites

The service life of composites is assumed to be strongly dependent on the bonding between the resin matrix and reinforcing filler. This bond is greatly improved by addition of a coupling agent which is usually applied at the surface of the filler.

The objective of this study was to determine 1) the nature and extent of interaction with the filler and resin achieved by the silane coupling agent, 2) what mode of application of the coupling agent produces optimum bond formation, 3) the extent of debonding that may occur on storage in a simulated oral environment and, 4) the improvement in physical or wear properties of composites which may result from optimizing interfacial bonding.

Colloidal silica wafers were molded and subjected to various silanizing treatments for 2 hours. Formation of chemical bonding between the silica and the silane was determined from the disappearance of the free hydroxyl band of silica at 3740 cm^{-1} and the siloxane peak of the bulk silica at 1850 cm^{1} as internal infrared absorption standard. The effect of the solvent used for the 3-methacryloxypropyltrimethoxysilane (MPTS) as well as the effect of the addition of 2% n-propylamine to the reaction mixture are given in Table 11. Treatment with silane dissolved in various solvents yielded silica surfaces which generally had a reduced free hydroxyl absorption band. A high percentage of bond formation occured in 50% ethanol. Initial reduction of the hydroxyl absorption was also large when dimethylsulfoxide or dimethylformamide were used as solvents. However, on standing of the sepcimens in air this value increased again, probably due to the hydrolysis of an unstable complex of silica with these solvents which was also observed from spectroscopic data when silica was exposed to the respective solvents. Little or no bond formation took place on treating the silica with silane dissolved in acetone (in which the silane may decompose on standing) or toluene. Addition of n-propylamine greatly increases the coupling effectiveness of the silane studied. Complete elinimation of the free hydroxyl band occurs when acetone, n-pentane or cyclohexane are used as solvents in the presence of n-propylamine.

The stability of the bonding was studied by aging specimens at 68°C for 280 hours. Most water-stored specimens showed a considerable increase in the free hydroxyl present indicating a hydrolytic fission, i.e. a reversal of the silanization (Table 12). However, no reappearance of the hydroxyl band was observed for silica modified with silane dissolved in cyclohexane in the presence of n-propylamine. Thus, under these conditions a stable bond is formed.

The silanizing reaction is also influenced greatly by the type of amine used as catalyst. Optimum bonding was obtained with n-propyl

TABLE 11

EFFECT OF SOLVENT AND n-PROPYL AMINE ON CHEMICAL BONDING OF SILANES TO SILICA SURFACES

Silane: 2 vol % solution of A-174 (3-methacryloxypropyltrimethoxysilane)
Reaction Time: 2 hours at room temperature.

	Bonding, %[a]	
Silane Solvent	No Catalyst	2% n-Propyl Amine
0.05 Vol % Acetic Acid (pH = 3.6)[c]	31.5	b
0.05 Vol % Acetic Acid (pH = 3.6)[d]	32	b
20% Ethanol-80% H_2O (pH = 3.6)	2	b
50% Ethanol-50% H_2O (pH = 3.6)	53	b
95% Ethanol	13	70
50% Acetone-50% H_2O	31	b
90% Acetone-10% H_2O	23	100
Acetone[e]	0	100
Dimethylsulfoxide	89 (48.5)[f]	41.5
Dimethylformamide	48.5	78.4
n-Pentane	33.5	100
n-Hexane	26.5	85
Cyclohexane	26.5	100
Toluene	4	70

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[a] Calculated from relative intensity ratio of infrared absorption peak at 3740 cm^{-1} (free OH band) and around 1850 cm^{-1} (siloxane linkage in the bulk of the silica). Samples were washed with acetone for 15 minutes and air-dried prior to infrared measurements.

[b] Solution became cloudy on addition of n-propylamine.

[c] Silane was hydrolyzed in 0.05 vol % acetic acid for 7 days prior to reaction with silica.

[d] Silane was hydrolyzed in 0.05 vol % acetic acid for 1 hr. prior to reaction with silica.

[e] Solution decomposes on standing.

[f] Numbers in parentheses indicate change in absorption at 3740 cm^{-1} of wafer after 1 hour.

TABLE 12

STABILITY OF SILICA-SILANE BOND

After silane treatment silica wafer was stored in water at 68°C for 280 hours.

Silane Solvent	% n-Propyl Amine in Solvent	Bonding, %[a]	
		Before Storage	After H_2O Storage
95% Ethanol	-	9	0
95% Ethanol	2	70	14.5
50% Ethanol (pH = 3.6)	-	12	0
20% Ethanol (pH = 3.6)	-	2	0
Acetone	2	100	26.5
90% Acetone-10% H_2O	-	23	20
90% Acetone-10% H_2O	2	100	41.1
Dimethylsulfoxide	-	75[b]	0
Dimethylsulfoxide	2	100[b]	26.5
Dimethylformamide	-	17.7[b]	17.5
Pentane	-	33.5	33.5
Pentane	2	100	71.5
n-Hexane	-	33	9
n-Hexane	2	85	34
Cyclohexane	-	26.5	0
Cyclohexane	2	100	100
Toluene	-	4	0
Toluene	2	70	38

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[a] Calculated from relative intensity ratio of IR peaks at 3740 cm^{-1} and 1850 cm^{-1}.

[b] Bonding decreased on standing.

or diethylamine (Table 13). Tertiary aliphatic amines are less effective. The aromatic N,N-dimethyl-p-toluidine and a heterocyclic amine (pyridine) characterized by much lower basicities, were less effective catalysts.

Improvement in the strength of a composite prepared from colloidal silica silanized in the presence of n-propyl amine (PA) is shown in Table 14. This composite had a tensile strength of 23.3 MPa as compared to 4.7 MPa for a composite prepared from pastes containing SiO_2 silanized without PA. A concentration of 2% PA is most effective for silanizing glass powder. The resulting composites have excellent mechanical properties (tensile strength 51.6 MPa, compressive strength 278 MPa) which is respectively 10% and 26% higher than is obtained with glass silanized in the absence of PA (Table 15). The tensile and compressive strengths of composites containing the glass treated with the coupling agent and amine were not reduced by storage in 60°C water for 3 days or on thermocycling in 5° and 55°C water for 6 days. Thus silanization of the substrate in cyclohexane containing 2% PA yields materials with an increased strength which is maintained on storage.

E. Peroxy Esters and Hydroperoxides as More Storage Stable Initiators for Composite Resins

A deficiency of commercial dental composites formulations is their limited storage stability. The constituents, especially the initiator-containing pastes, often harden prior to use. Alternatively, the curing time of the mixed pastes either becomes too long for clinical applications or mixes do not harden at all. The main cause for this storage instability is the benzoyl peroxide component. Replacement of this initiator by other peroxides (e.g. hydroperoxides or peroxy esters) with longer thermal half-life decomposition values appeared to be desirable.

TABLE 13

EFFECT OF AMINES IN THE SILANIZATION OF SILICA SURFACES

Silanizing solution: 2 vol % silane* and 2 vol % amine in cyclohexane.
Reaction time: 2 hours at room temperature.

Amine	Base Ionization Constant	Bonding, %[a]
n-Propylamine	3.8×10^{-4}	100
Diethylamine	9.5×10^{-4}	100
Triethylamine	5.5×10^{-4}	49.5
Tri-_n_-butylamine	8.52×10^{-5}	49.3
N,N-Dimethyl-_p_-toluidine	1.1×10^{-9}	20.5
Pyridine	2.3×10^{-9}	0

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[a] Calculated from relative intensity ratio of IR peaks at 3740 cm^{-1} and 1850 cm^{-1}.

* 3-methacryloxypropyltrimethoxy silane

Table 14

EFFECT OF SILANE (A-174) TREATMENT ON HARDENING TIMES AND ON THE TENSILE STRENGTH OF A PASTE-PASTE COMPOSITE

Composition of Composite

	Initiator paste % by weight	Catalyst paste % by weight
BIS-GMA	53.62	53.88
TEGDMA	22.99	23.11
BHT	0.154	0.154
Benzoyl peroxide	0.766	- -
Dimethyl-p-toluidine	--	0.386
Filler	22.47	22.47

Equal weights of initiator and catalyst paste were used.

Properties

	Cabosil Filler Treatment	
	1% (vol) silane in C_6H_{12}*	1% (vol) silane + 1% n-propylamine in C_6H_{12}*
Hardening time at 23°C, in minutes	5	3
Tensile Strength, MPa	4.7 ± 0.7	23.2 ± 0.9

* Cyclohexane

Table 15

EFFECT OF SILANIZING TREATMENT OF GLASS FILLER ON PROPERTIES OF DENTAL COMPOSITE

Composition of Composite

Powder: Silanized Corning Glass 7724, coated with 1% benzoyl peroxide
Liquid: (85.1% BIS-GMA, 14.9% BGDMA) plus 0.23% N,N-dimethyl-p-toluidine and 0.2% BHT
Powder/liquid ratio: 3/1

	Silanization (0.5% A-174 in C_6H_{12}*plus n-propylamine):				
	0%	0.5%	1%	2%	3%
Setting Time, minutes	4 1/2	3	3	2 1/2	3
Tensile Strength, MPa					
24 hours in 37°C water	46.9±2.0	47.8±1.2	45.7±3.6	51.6±6.0	45.9±4.8
3 days in 60°C water	47.9±1.7	48.4±3.2	-	50.8±2.5	-
6 days cycling 5-55°C	46.1±2.9	47.9±3.3	-	53.6±1.4	-
Compressive Strength					
24 hrs in 37°C water	221±24	243±14	241±13	278±13	216±19
3 days in 60°C water	247±22	284±14	-	281±19	-
6 days cycling 5-55°C	249±13	282±10	-	288±13	-
H_2O sorption mg/cm^2	.62±.02				

* Cyclohexane

It was the objective to determine the reactivity of more stable peroxides with currently used amines, and the rapidly reacting amines synthesized in our laboratory. More stable initiators investigated were t-butyl peroxymaleic acid (TBPM), 2,5-dimethyl-2,5-bis (benzoyl peroxy) hexane (DMBPH) and cumene hydroperoxide (CHP). The TBPM proved to yield composite formulations with much lower setting times than those obtained with DMBPH. Materials cured with CHP as initiator hardened but the resulting composites were of undesirable shades. Results of setting time tests indicated that composite formulations containing 4% TBPM and from 1.5 to 3.0% DEAPAA required from 16 to 21 min to cure, those containing 2.5% dimethylamine or diethylaminophenethanol, 6.5 and 7.5 min, respectively. Faster curing times of 4, 4.5 and 2.5 min. were found when 2.5% dimethyl-p-toluidine (DMPT), 2.5% aminophenethanol or 2.5% p-toluidine were used as accelerators. However, the shades of the resulting composites were not considered to be satisfactory for dental restoratives. The cure and physical properties of the more promising TBPM-containing formulations are given in table 16. Generally in the presence of primary or secondary amines a fast set is obtained but the former yields resins with darker shades whereas the latter amines give materials with poor strength, but the cure is somewhat faster. With 3% TBPM and 2.5% DMPT, composites with satisfactory strength are obtained (Table 16). Thus, all but the MPT-containing formulations pass the requirements of ADA Specification No. 27, but had lower mechanical properties than similar compositions cured with benzoyl peroxide.

The storage stability of the components of these composites is, quite unexpectedly, not better than that of typical commercial composites.

TABLE 16

Properties of Composites Cured with t-Butylperoxymaleic Acid (TBPM) Initiator

Powder: Corning Glass 7724, silanized and coated with TBPM.
Liquid: 70% BIS-GMA - 30% 1,10-decamethylene glycol dimethacrylate, 2.5% amine and 0.1% BHT.
Powder-Liquid Ratio: 3 to 1

Amine	Setting Time (min)	Strength Tensile (MPa)	Strength Compressive (MPa)
	4% TBPM Initiator		
t-Butyldimethylaniline	7-7.5	38.5 ± 2.9	210 ± 9
Methyl ester of p-tolyl-glycine	3-3.5	28.4 ± 2.1	157 ± 4
N-Methyl-p-toluidine (MPT)	4-4.5	28.4 ± 2.2	162 ± 5
Dimethyl-p-toluidine (DMPT)	6.5-7	38.1 ± 3.6	209 ± 11
	3% TBPM Initiator		
2.5% DMPT	6	41.8 ± 2.2	223 ± 10
2.3% DMPT + 0.2% MPT	5-5.6	41.6 ± 1.0	223 ± 4
2.2% DMPT + 0.35% MPT	5-5.5	40.6 ± 3.8	222 ± 4
1.5% DMPT + 1% MPT	5	37.6 ± 3.6	200 ± 9
2.5% MPT	4-4.5	28.4 ± 2.2	162 ± 6

From the larger thermal half-life decomposition time of TBPM versus benzoyl peroxide one would expect a greater storage stability of the system containing the former initiator. A composite formulation from a TBPM coated glass powder mixed with room temperature-stored monomer showed a 25% increase in setting time after 48 hour storage of the powder at 60°C. The higher percentage of TBPM on the glass surface (3% vs. 1% for benzoyl peroxide) may be responsible for the increased deterioration of the initiator. This peroxy-ester may hydrolyze in air at elevated temperatures resulting in the longer cure. Furthermore, the monomeric BIS-GMA/diluent ingredients of the resin gel within a few days when stored at 60°C, probably because of the large concentration of amine (2.5% vs. about 0.25% for a benzoyl peroxide-initiated composition). These results indicate that peroxyesters are not particularly suitable initiators to increase the storage life of composites.

F. Autocurable Polymer Blends as Routes to Improving Chemical and Mechanical Properties of Denture Base and Other Dental Materials

The polymer blend approach is being pursued rigorously to improve industrial plastics for specialty applications and may provide a route to improving dental resins. Our interest specifically is in exploring this approach as a means of achieving tougher but not significantly less strong dental resin systems.

A copolymer (PVF$_2$-TFE) consisting of 27% tetrafluoroethylene (TFE) and 73% of vinylidene fluoride (VF$_2$) was dissolved to the extent of 5% by weight in methyl methacrylate (MMA) containing 0.5% dimethyl-p-toluidine (DMPT). This liquid was mixed with 2 parts by weight of poly(methyl methacrylate) PMMA, containing 3% benzoyl peroxide. The blend cured well in 15 minutes at 37°C in a 100% relative humidity chamber and the diametral tensile strength results (25 MPa) were comparable to the control (28 MPa). At least at the 5% PVF_2-TFE level this blend does not adversely affect curing time or strength and its less brittle nature is a step in the desired direction.

G: Status Report - The Desirability of Using Radiopaque Plastics in Dentistry

Ideally any material used in the mouth or in the dental operatory should be radiopaque. A motion by the House of Delegates of the American Dental Asssociation to require that all dental plastics possess this property resulted in the preparation of a status report. An extensive library research including computerized search for foreign bodies in the human body was conducted to determine the frequence of occurrence as well as the severity of episodes of the ingestion and inhalation of plastics of dental origin. Dates of accidents resulting from dental objects from 1972 to 1979 were obtained from the U. S. Consumer Products Safety Commission and were evaluated. The tentative summary and conclusions of the report were as follows:

(1) The widespread use of plastics in dental practice has increased the risk of ingestion, inhalation or of embedding of such materials in the soft tissues. The frequency of such accidents is relatively small compared to the number of plastic materials or appliances used. Nevertheless, the severity of such incidents may make it mandatory to rapidly locate, diagnose and remove such foreign bodies. The need for immediate removal and assurance of total retrieval of ingested, aspirated and embedded plastic

materials suggests that plastics of sufficient x-ray radiopacity be used, or if necessary, be developed, wherever an intraoral application is anticipated.

(2) The following recommendations for specific types of dental application were suggested:

a. Restorative Materials

Radiopaque composites with properties comparable to those of translucent products are marketed commercially and are the materials of choice for anterior restoratives. Adding a radiopacity requirement to Specification No. 27 for Direct Filling Resins would encourage their usage.

b. Temporary Bridge and Crown Materials

Radiopacity for temporary bridge work and crowns is highly desirable. Such material is available which appears to have adequate physical and clinical properties. Whenever special factors point to the possibility of loss of adhesion or fragmentation of the appliance a radiopaque material is indicated.

c. Denture Base Materials and Plastic Teeth

Radiopaque denture base materials and plastic teeth, combining adequate physical, biocompatible and esthetic properties with ease of processing and finishing similar to the acrylic plastics most commonly used, are not available commercially. Porcelain teeth when mechanically interlocked in heat-cured (composite) radiopaque denture resin will be weakened or fractured. A satisfactory radiopaque resin tooth has not been developed. To overcome present deficiencies further studies to incorporate radiopaque glass fillers or novel techniques to synthesize radiopaque resins should be explored. Even if the technical difficulties of redesigning porcelain teeth or of manufacturing radiopaque resin teeth could be overcome, the initial production and stocking of such teeth would run into millions of dollars and would probably require several years to accomplish. In the interim period the commercial availability of a non-toxic radiopaque denture base formulated according to the existing "state of the art" should be encouraged. The use of such a product is indicated for patients with a high risk of accidental ingestion due to neuromuscular, epileptic, asthmatic, mental or other health or occupational problems, where the decreased danger of injury caused by the appliance far outweighs its somewhat poorer physical and esthetic properties.

d. Impression Materials

The need for radiopacity in impression materials has been clearly established. Inclusion of this requirement in existing American Dental Association specifications may require some changes in formulation of present materials. There may be delays in establishing a test procedure, because of the difficulty in determining quantitatively the radiopacity of materials and its relevancy to clinical practice. The advisability of adding at an early date an ad interim semiquantitative requirement for radiopacity of impression materials should be considered.

e. Development of Radiopaque Standards

Investigation to standardize techniques for the reproducible measurement of the radiopacity of dental materials should be encouraged. The primary goal of these investigations should be the development of satisfactory standards that correlate with clinical needs.

H. Improving Dental Cements

Chelating agents such as eugenol react with zinc oxide to form cementitious materials which, because of their excellent tissue tolerance, have found many applications in dental practice. However, their mechanical properties as well as their hydrolytic instability are factors limiting their use as longer lived temporary restorations.

The initial objective of this study was to (1) synthesize 2-methoxyphenol (guaicol) derivatives such as 2,5-dimethoxyphenol (DMP) and esters of vanillic (4-hydroxy-3-methoxybenzoic acid) or its isomers which are liquids at room temperature, (2) study their reaction with metal oxides and (3) evaluate the properties of the resulting cements.

2,5-Dimethoxyphenol (DMP) was obtained by diazotization of 2,5-dimethoxyamiline with $NaNO_2$ in dil H_2SO_4, similar to the procedure of Astill, Fassett and Rondabush (Biochem. J. <u>72</u>, 451, 1959).

By substituting DMP for eugenol the setting time of a commercial ZOE powder mix was reduced from 4 min to 30 sec. Properties of cements prepared from various compositions made from DMP, o-ethoxybenzoic acid (EBA) or eugenol are shown in Table 17. Presence of EBA speeds up

Table 17

Properties of Cement Prepared from 2,5-Dimethoxyphenol

Powder: 64% ZnO, 30% Al_2O_3, 6% hydrogenated rosin
Powder-liquid ratio: 1.7 g/ 0.2 ml

Concentration of Liquid			Setting Time	Compressive Strength
EBA[a]	DMP[b]	EUG[c]	(min)	MPa
80	20	-	6.5	56.0 ± 4.7
62.5	37.5	-	6.5-7	47.7 ± 0.8
50.0	50.0	-	5.5	36.9 ± 0.3
41.7	33.3	25.0	3.5-4	52.4 ± 3.6
62.5	-	37.5	4.5-5.5	81.3 ± 15.5
-	50.0	50	∿ 30	-

[a] o-ethoxybenzoic acid

[b] 2,5-dimethoxyphenol

[c] eugenol

setting time and improves strength which is considerably higher than that of zinc oxide eugenol, but somewhat lower than that of EBA cements. Thus DMP cements may be useful where cements with properties intermediate to those of ZOE or EBA are desired provided DMP has the same biocompatibility as the structurally related eugenol.

Hexyl 4-hydroxy-3-methoxybenzoate (hexyl vanillate, HV) was synthesized from vanillic acid, n-hexanol in the presence of p-toluene sulfonic acid. After refluxing for 26 hours and distilling under reduced pressure 24.5 g. of product was obtained. An initial HV-ZnO mix required several hours to harden. The setting time was reduced greatly when EBA-HV liquid was employed. Whereas eugenol, and to a much lesser extent DMP, inhibit polymerization of composite formulations, HV does not retard this reaction. (Table 18). Hence, HV containing (non-eugenol)cement will be further studied for possible use with composite resins.

Table 18

Inhibition of the Polymerization of Composites by Phenolic Compound

Composite: Adaptic
Phenolic compound was added to the mix

Percent Phenol in Mix	Setting time, min.	Comments
-	4.5	-
5% Eugenol	does not harden	Yellow-brown
5% DMP	" " "	Pink
1% DMP	90	Soft set, dark pink red
1% HV	4.5	-
0.1% Eugenol	∿ 30	Soft, slightly yellow
0.1% DMP	∿ 15	Pink
0.1% HV	4.1	-

II. Development of Adhesive Bonding Techniques

The objective is to develop a basis for clinically applicable adhesion techniques suitable for bonding polymer materials to mineralized tissues, e.g. dentin and bone. A clinically acceptable technique which establishes durable adhesive bonding between calcified tissues and dental restorative and sealant materials probably would not only reduce significantly the incidence of secondary caries that can arise from microleakage between restorations and tooth surfaces, but it would also lead to a greater preservation of sound tooth structure through the increased use of conservative dental therapy.

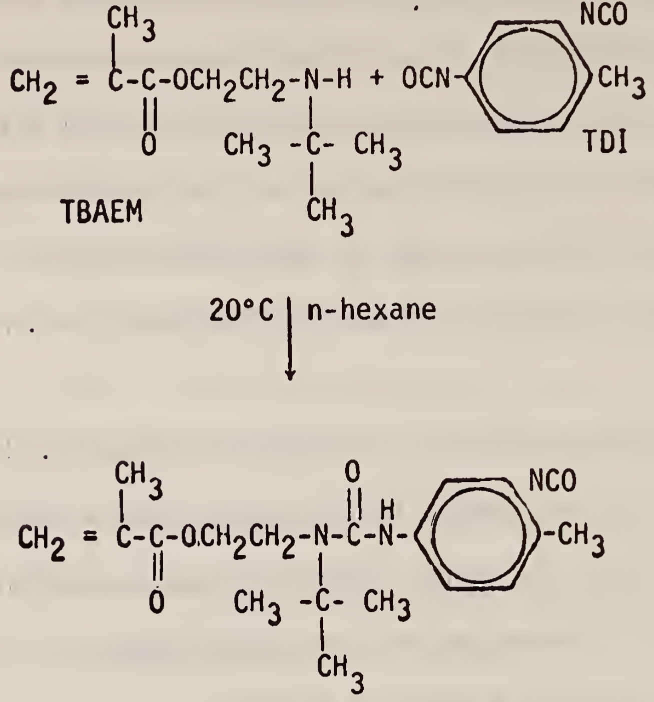
One approach toward achieving such effective adhesion involves the design of suitable coupling agents that can form stable chemical bonds between the polymers used in dental preventive and restorative materials and one or more of the components of hard tooth tissue.

A. Adhesion Promoting Functional Monomers

1. Isocyanate Urea Methacrylates

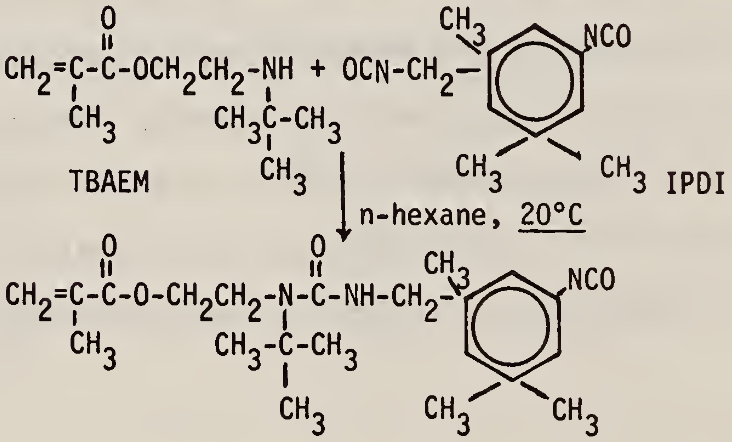
The well known reactivity of organic isocyanates with compounds having active hydrogens (e.g. $-OH$,$-NH_2$, etc.) and the latent presence of such groups in dentin suggested the synthesis of urea methacrylates with pendant isocyanate groups as potential adhesion-promoting functional monomers. The syntheses of two isocyanato urea methacrylates are conveniently effected by the controlled reaction of <u>N-tert</u>-butyl-2-aminoethyl methacrylate (TBAEM) and diisocyanates that have isocyanate groups of different reactivities such as toluene diisocyanate and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, usually identified as isophorone diisocyanate (IPDI).

The isocyanato urea methacrylate, TBAEM-TDI, a white solid, was derived from N-t-butyl-2-aminoethylmethacrylate (TBAEM)and toluene diisocyanate (TDI) by the route shown below



TBAEM-TDI

Similarly, we have prepared a liquid isocyanato urea methacrylate from TBAEM and IPDI as shown below:



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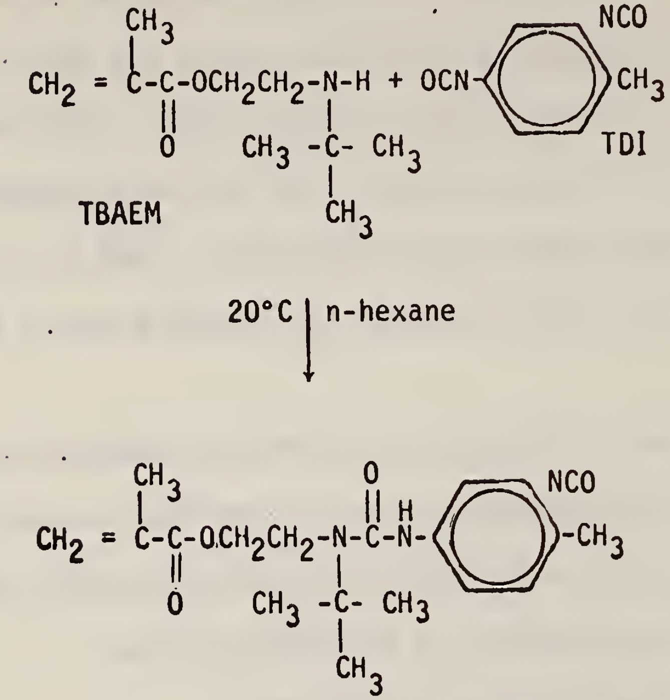

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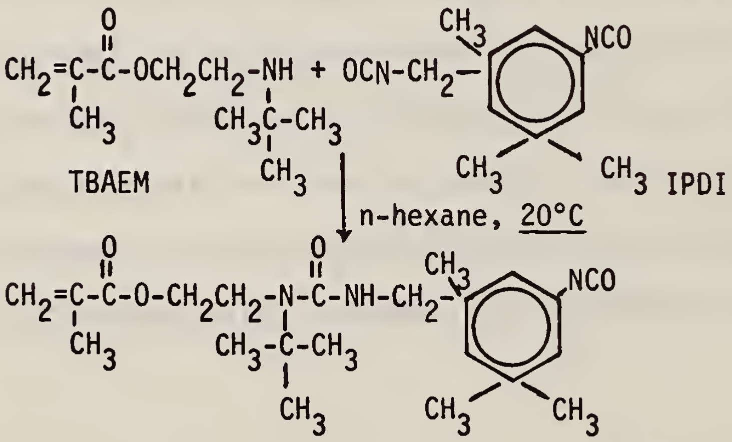

TBAEM-IPDI

These materials have been produced in sufficient quantity for characterization measurements and for evaluation of their adhesion-promoting ability to bone and dentin.

B. Surface-Active Amine Accelerators as Adhesion Promotors

Another type of potential adhesion-promoting agent under study is the surface active amine accelerator. Our study of the effect of surface-active amine accelerators on hydroxyapatite-(HA) filled composites has been extended to include 4-N,N-dimethylaminobenzoic acid (4-DMAB) and 3-N,N-dimethylaminobenzoic acid (3-DMAB). By determining the influence of coupling agents on the strength properties of a HA-filled composite, an estimate of the usefulness of a substance as a potential adhesive bonding agent can be made. HA containing preadsorbed 4-DMAB (2.3%) prepared by Dr. Misra of this laboratory was used in the preparation of composite specimens for a formulation of BIS-GMA (7)/TEGDMA (3) containing 1% BP and 0.06% tyrosine. The setting times and diametral tensile strength were determined and are given in Table 19 (Formulations VI and VII). Some of the previous results are shown for comparison.

In Table 20 are shown the results for HA composites prepared by paste/paste formulations and using 4-DMAB (H, I) and 3-DMAB (J, K) dissolved in the monomer system rather than preadsorbed onto HA. The DTS of the composites are considerably higher for 4-DMAB in these formulations (H, I) compared to those obtained with formulation VI (Table 19). Table 21 is an attempt to devise a control applicable to these HA-filled composites using a very effective amine accelerator (DMSX) that has virtually no surface-active character. The DTS results for HA composites formulated with DMSX were significantly lower than those obtained using dissolved 4-DMAB and 3-DMAB.

TABLE 19

Setting Times and Diametral Tensile Strengths of HA-Filled Composites* Using Adsorbed Surface-Active Amines

Formulation	Monomer System	HA	P/L	Setting Time (min)	Diametral Tensile Strength MPa ± Std.Dev. (No. of Specimens)
I	BIS-GMA(7) TEGDMA (3) BP = 1% TYR = 0.1%	DMAPAA = 1.9%	5/6	very fast <1.0	19.9 ± 4.9 (4)
II	Same as I but BP = 0.25% and TYR = 0.05%	Same as I	2/3	1.75	24.5 ± 6.6 (4)
III	Same as I but TYR = 0.07%	DMAPAA = 0.18%	2/3	3.0	21.6 ± 2.7
IV	Same as I	4-DMAS = 2.4%	2/3	5.0	24.1 ± 5.4 (5)
V	Same as I but BP = 2.1% and TYR = 0.1%	4-DMAS = 2.4%	2/3	3.0	23.2 ± 2.9 (4)
VI	Same as I but TYR = 0.06%	4-DMAB = 2.3%	2/3	5.0	21.5 ± 7.4 (6)
VII	Same as VI but stored at 37°C and 100% relative humidity for 72 hours rather than 24 hours				19.8 ± 4.1 (5)

* Composites prepared by powder/liquid technique

TABLE 20

Setting Times and Diametral Tensile Stregnths of HA-Filled Composites* Using Dissolved Surface-Active Amine Accelerators

Formulation	Peroxide Paste	Acc. Paste	P/L	Setting Time (min)	Diametral Tensile Strength MPa ± Std.Dev. (No. of Specimens)
A	BIS-GMA(7) TEGDMA (3) BP = 1% TYR = 0.1%	BIS-GMA(7) TEGDMA (3) POLYSAM-1 = 1%	5/6	<1 min fast	20.9 ± 1.5 (4)
B†	Same as A	POLYSAM-1 = 0.5%	2/3	~10.0	36.5 ± 4.4 (4)
C	Same as A	DMAPAA = 0.18%	2/3	3.0	22.3 ± 5.2 (5)
D	Same as A BP = 0.25% TYR = 0.05%	DMAPAA = 0.18%	2/3	8.0	31.9 ± 3.7 (4)
E	Same as A but TYR - 0.06%	DMAPAA = 0.36%	2/3	1.0	23.2 ± 4.6 (6)
F†	Same as A	4-DMAS = 0.36%	2/3	15.0	16.9 ± 2.7 (5)
G†,a	Same as A	A-4-DMAS = 0.5%	2/3	17.0	34.0 ± 8.4 (5)
H†	Same as E	4-DMAB = 0.5%	5/6	16.0	28.8 ± 1.5 (4)
I†	Same as E	4-DMAB = 0.5%	2/3	17.0	31.8 ± 0.9 (4)
J	Same as E	3-DMAB = 0.5%	5/6	5.5	28.0 ± 0.9 (5)
K	Same as E	3-DMAB = 0.5%	2/3	6.0	28.8 ± 3.1 (4)

* Composites were prepared from equal parts of peroxide and accelerator paste
† Cured in mold for 20 minutes instead of the usual 15 minutes
a Formulation G was stored for 72 hours in 100% humidity bath at 37°C

Formulation 0 of Table 21 which is for unfilled resin but using the same catalyst and other ingredients also gave DTS values significantly higher than those prepared with HA filler. Apparently the uncoated HA can act to reduce the tensile strength of the BIS-GMA copolymer, perhaps by introducing defect sites in the organic matrix.

As a method for assessment of the adhesion potential of these surface-active amine accelerators, comparative diametral tensile strength measurements, performed on hydroxyapatite filled composites, did not yield results as definitive as those obtained from similar measurements comparing the strengths of silanized and unsilanized glass composites. Nevertheless, the results of this study indicate that some surface-active amine promotors, under some conditions, can lead to improved adhesion of dental restorative or sealant materials to apatitic surfaces.

A manuscript entitled"The Accelerative and Adhesive Bonding Capabilities of Surface-Active Accelerators" was submitted to Journal of Dental Research for publication.

C. Literature Survey of Reactive Adhesives with Potential for Dental Application

The possible usefulness of dental applications of "reactive adhesives", which have been suggested in the patent literature for bonding various metals at room temperature has been investigated. These adhesives are based on two component systems that are brought together when two substrates treated with these components contact each other. The components react to produce a chemical cure within a few minutes.

The adhesive is usually prepared by dissolving an elastomer in a monomer or oligomer solution. Curing is by a free radical mechanism and rapid polymerization occurs. The cured system is toughened by the elastomeric domains which are incorporated into the structure by grafting.

Table 21

Setting Times and Diametral Tensile Strengths of

HA-Filled Composites* Using DMSX†

Formulation	Peroxide Paste	Acc.Paste	P/L	Setting Time (min)	Diametral Tensile Strength MPa ± Std.Dev. (No. of Specimens)
L	BIS-GMA(7) TEGDMA(3) BP = 1% TYR = 0.1%	BIS-GMA(7) TEGDMA(3) DMSX = 0.23%	5/6	4.0	23.7 ± 1.7 (5)
M	Same as L	Same as L	2/3	2.0	23.2 ± 2.6 (5)
N	Same as L but TYR = 0.06%	Same as L	2/3	1.5	21.7 ± 1.4 (5)
O[a]	Same as N but no HA	Same as L but no HA	---	2.0	30.7 ± 3.8 (6)

* Composites were prepared using equal parts of peroxide and accelerator paste

† DMSX = N,N-dimethyl-sym-xylidine, a non-surface-active accelerator used here to provide a control for the investigation of surface-active accelerators.

[a] Unfilled resin, prepared from equal parts of BIS-GMA(7)/TEGDMA(3) with 1% BP and 0.06% TYR, and the same monomer system with 0.23% DMSX

In our initial studies formulations similar to those described by Wolinski (U.S. patent No. 3,994,764) were used which are made from soluble polyurethanes, acrylic or methacrylic acid and methyl methacrylate monomers, benzoyl peroxide initiator and an inhibitor such as butylated hydroxytoluene (BHT). The second component is a solution of amine accelerator with which the substrate surfaces (bone) are treated prior to application of the urethane-monomer component. In this exploratory work adhesion between flat bone substrates in air, 100% relative humidity and on storage in water was evaluated.

Problems in developing suitable formulations involved selecting a urethane which was completely soluble in the monomers. A commercial polyurethane (Estane 5712) which is claimed to be a reaction product of tetramethyleneglycol ethers of varying molecular weight and methylene diisocyanate was found to be monomer soluble.

Initial formulations cured much too slowly at room temperature to be clinically useful. On employing high concentrations of accelerator the viscous adhesives cured within 30 minutes which is still too slow for clinical application. Partial substitution of a dimethacrylate (decamethylene dimethacrylate, DMDMA) increased the reactivity so that bonding occurred within the period of several seconds to three minutes. In order to use urethanes other than Estane which does not have pendant isocyanate groups,efforts were made to replace acrylic acid by monomers which do not contain carboxylic acid groups. Highly viscous solutions of Estane in DMDMA and methyl methacrylate resulted. Substitution of isodecyl acrylate and isobutyl methacrylate for methyl methacrylate gave monomer mixtures in which the Estane polyurethane was not soluble.

Other changes in the compositions of the solutions were made to study the effect of the following parameters on the characteristics of the reactive adhesive formed and the resulting bone-to-bone bond: (1) ratio of DMDMA to methyl methacrylate concentration, (2) substituting other monoacrylate or monomethacrylates for methyl methacrylate, (3) replacement of acrylic acid by other monomers not containing carboxylic acid groups, (4) changes in the amine accelerator or solvent used.

Curing of the adhesive occurred for all compositions in which the urethane was soluble. Good adhesion between the substrates was obtained in air. However, for most formulations, debonding occurred quite rapidly in an aqueous environment. Most joints broke fairly readily after storage for 3 hours at 37°C and 100% RH or after storage in water. A joint prepared from a reactive adhesive formulation composed of 33% Estane, 33% DMDMA, 17% acrylic acid, 17% methyl methacrylate, 0.04% BHT and 3.6% benzoyl peroxide in which the substrate had been treated with 10% alcoholic dimethyl-p-toluidine did not debond on extended storage in water. Preliminary results do not indicate whether substrate treatment with 10% dimethyl-p-toluidine dissolved in ethanol or 1,6-hexamethylene glycol dimethacrylate or 10% dimethyl aminophenylacetic acid in ethanol yields adhesives with better bond strength. The latter amine was employed because it can be absorbed irreversibly on dentin from non-polar solvents.

Estane was found to be soluble in DMDMA-methyl methacrylate. Such monomer mixtures may prove useful as vehicle for adhesives containing polymerizable molecules with residual isocyanate groups which react with active hydrogen. Thus the reaction product of isophorone diisocyanate and tert-butylaminoethyl methacrylate (IPDI-TBAEM) previously synthesized in this laboratory does not dissolve benzoyl peroxide. To evaluate the adhesive characteristics of this compound the following composition was prepared: 30% IPDI-TBAEM, 30% DMDMA, 40% methyl methacrylate, 3% benzoyl peroxide, 0.4% BHT. Bone treated with amine accelerator and this composition gave a joint that readily separated on storage in a 100% RH environment.

D. Dental Tissue Debris Cleansing, Toxicity and Adhesion

The work conducted on our suggestion by McInnes and Clayton Jones of the Unvierstiy of Witwaterstrand, South Africa, to evaluate the cleansing effects of very dilute acid solutions and to determine the response of the underlying pulpal tissues to these acid solutions was completed. The pulpal responses elicited by 1% and 0.1% citric acid solutions in unlined and Dycal lined cavities after acid application were compared. The pulpal responses were evaluated in the permanent maxillary and mandibular incisors in 48 monkeys using labial class V cavities. Most severe pulpal responses were obtained with 1% aqueous and 1% dilute alcoholic citric acid solution-treated cavities followed by a silicate cement. Based on these results the use of these dilute acids to remove the smear layer and improve bonding to dentin, as was suggested in our previous *in vitro* work with 2-cyanoacrylate adhesives, cannot be recommended. The possible combination of Dycal with acid treatment to eliminate poor tissue response and yet obtain at least adequate temporary bonding is to be examined.

III. Wear Resistance and Mechanical Properties of Dental Materials

The principal immediate objective is to develop, or make use of, appropriate techniques to measure wear resistance and mechanical properties of dental materials and to use the forthcoming data as performance indicators to predict in vivo durability of these materials. The completion of the development of these methods to a satisfactory state is particularly important because of the long times and efforts required for clinical evaluations. In order to accomplish this task, some fundamental research on wear and related mechanical properties is being done to obtain a better understanding of the relevant degradation processes. This information will be of use in determining the principal variables of influence from which appropriate modifications may be incorporated in the wear apparatus to obtain meaningful results. In addition, the improved understanding of ways in which specific mechanical properties of composite systems correlate with wear behavior is expected to be instrumental in developing more durable systems.

Two types of wear tests have been developed here which comprise a classical pin and disc apparatus and an erosion technique. Although these particular methods are not necessarily expected to be used as final performance indicators, they do give basic information relevant and possibly essential to the development of an appropriate durability test, as will be apparent in later sections of this report. Complementary efforts involve microdefect analysis using x-ray and optical microscopic observation of damaged regions made resolute by a silver staining technique. In order to obtain a relevant wear test we assert that the subsurface damage resulting from in vitro wear should resemble that obtained from in vivo worn specimens. Another aspect studied is the coupling between certain chemical solvents and wear. The following paragraphs describe the work performed during this fiscal year on wear and mechanical properties of dental materials.

A. Pin and Disc In Vitro Measurements

The pin and disc apparatus is completely automated comprising three identical rotating platforms containing the disc shaped specimens of the material to be investigated. The principal of operation is depicted by Figure 1. A stationary slider (pin) of human enamel, or appropriate substitute, impinges on each of the rotating specimens producing a wear track of 12 mm mean diameter. The slider is loaded with weights to obtain the desired normal stress which is usually 10 MPa. The depth of the wear track is measured periodically at 10 equally spaced positions along the track circumference using linear variable differential transformers with ruby tipped probes as shown in the figure. Distilled water at 37°C flows over the specimens to control temperature, lubricate, and wash away debris. Figure 2 is a close-up photograph showing the specimen and cup, wear pin and mounting collet, probes and transformer, and the thermocouple junction.

In this work the wear rate G (with respect to distance traveled) is defined as

$$G = V/LF \qquad (1)$$

Where V is the volume of material removed, L is the total track length, and F is the normal force or load. Using the relations $V = \pi abs$, $L = \pi an$,

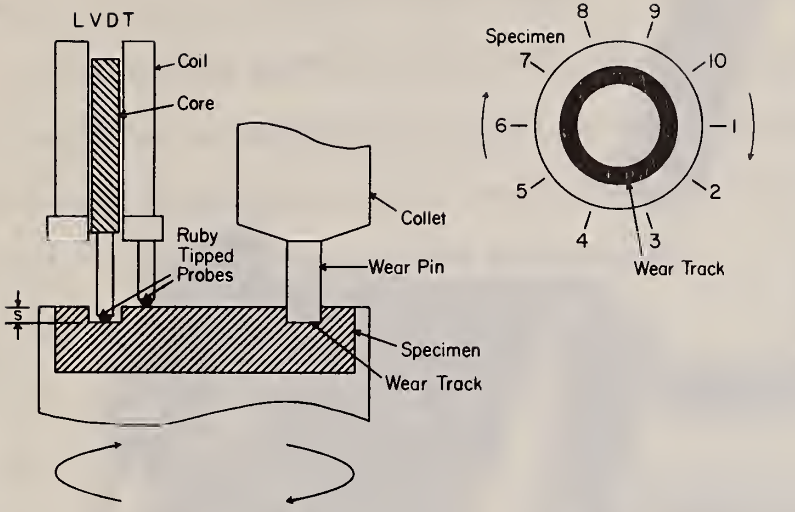

Fig. 1. Schematic illustration of principle of pin and disc measurement.

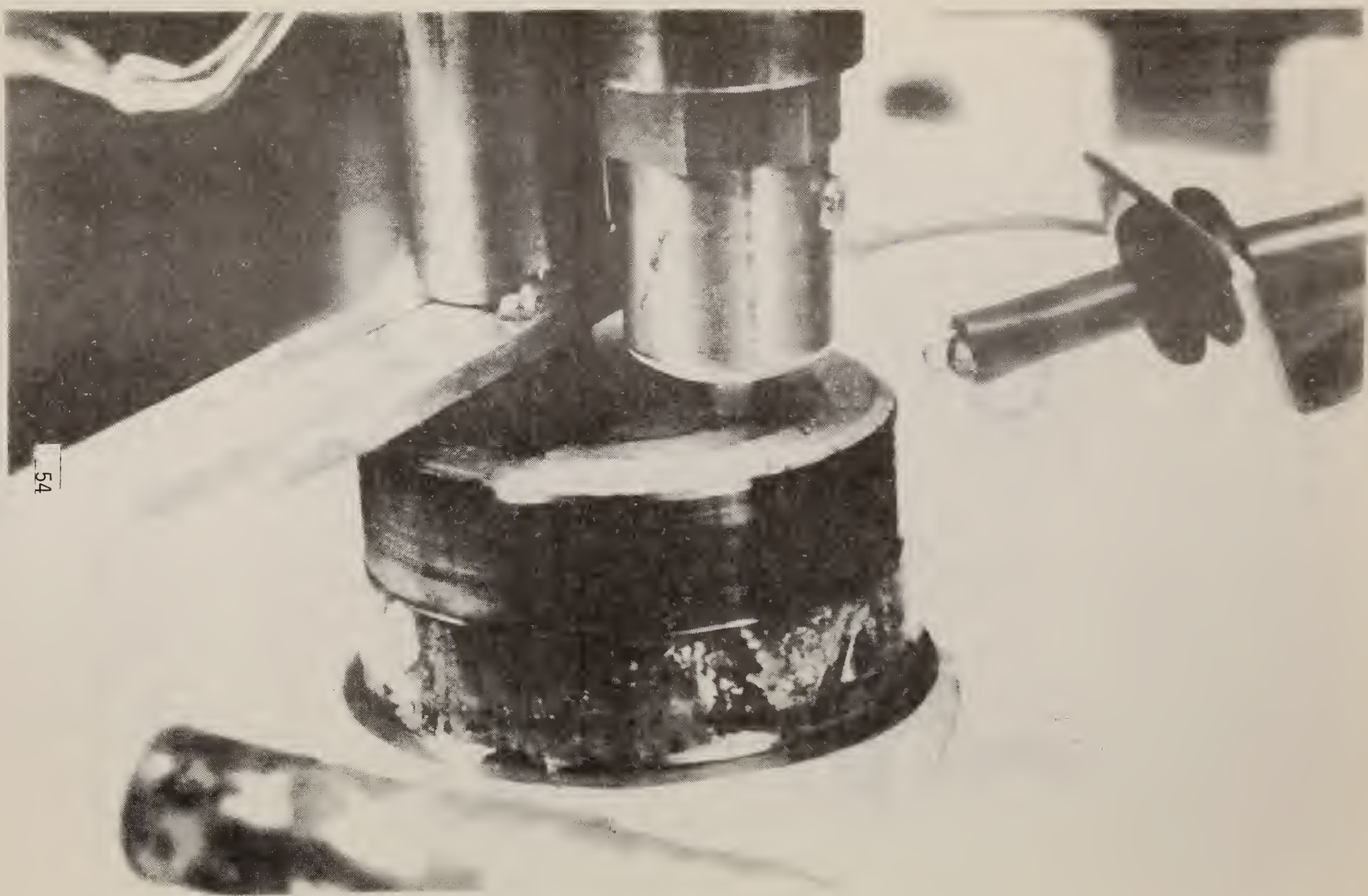

Fig. 2. Close-up photograph showing wear pin and mounting assembly, transformer assembly, and water jet nozzle.

and $F = \pi a^2/4$, where a and b are the wear pin and track diameters, respectively, s is the track depth, n is the number of revolutions and τ is the normal stress, the operating equation

$$G = 4m/\pi a\tau \tag{2}$$

is obtained from eq. (1). Eqs. (1) and (2) are equivalent only over a region where $m = ds/dn$ is constant with time.

A considerable portion of our activity over the past year has been devoted to obtaining an appropriate substitute for human enamel wear pins. Human enamel is objectionable in this application for the following reasons:

1. It is inhomogeneous and anisotropic.
2. Sample to sample variation is large.
3. Fabrication of wear pins is difficult.
4. It is chemically unstable.
5. Enamel layer is too thin for long time wear tests.

In view of these objections it is difficult to obtain, or even conceive of, high quality experimental procedure with so many additional variables of influence introduced through the use of enamel wear pins.

To date three possible substitutes for enamel have been investigated for which the results are given in Table 22. In addition to the wear rate G, two kinds of standard deviation are included to depict the irregularities observed in these measurements. σ_1 is obtained from the residuals about a linear regression over an apparent linear region of track depth versus revolutions data. σ_2 is obtained from the residuals about an average of G values over the 10 positions around the track circumference. (See Figure 1) Accordingly, σ_1 is a measure of the apparent irregularity of wear with time including experimental imprecision, whereas

σ_2 is presumably a measure of specimen inhomogenuity. Since σ_2 has always been found to be considerably larger than σ_1, it is apparent that additional improvements in experimental precision will not enhance the facility of this technique to evaluate dental materials.

TABLE 22

Summary of Wear Rates
Using Various Pin Materials

Couple	G TPa^{-1}	σ_1 TPa^{-1}	σ_2 TPa^{-1}
Velvalloy - Enamel	0.0518	0.00051	0.0064
- Durapatite*	0.0533	0.00049	0.0058
- Stainless Steel†	0.0488	0.00036	0.0055
- Sapphire	0.0795	0.00043	0.0051
Adaptic - Enamel	0.0106	0.000038	0.0014
- Durapatite	0.0084	0.00012	0.0032
- Stainless Steel	0.0615	0.00070	0.0036
- Sapphire	0.00416	0.00022	0.0026

* A form of sintered hydroxyl apatite made by Sterling-Winthrop Research Institute

† 18-8, 303 (austenitic)

Velvalloy and Adaptic were chosen as wear specimens because they were used in the three year clinical tests of Phillips and coworkers [5-7]. In their work based on deterioration of anatomic form, the amalgam was found to be superior to the composite. On the contrary, according to the results in Table 22, the composite displays superior in vitro wear performance when enamel, durapatite, or sapphire wear pins are used. With stainless steel pins, however, the wear increases markedly on the composite and a correlation, although very marginal, with the clinical tests is obtained. Although the results in the table show that either durapatite or sapphire is a good substitute for enamel, in vivo wear on restoratives from opposing enamel does not appear to be the most significant contributing factor to the degradation of restoratives.

When the values of G in Table 22 were plotted against the hardness of the wear pins, an interesting result was obtained as illustrated by Figure 3. With the amalgam the wear rate increases with increasing pin hardness displaying regular monotonic response as expected from a normal wear mechanism. With the composite an inverse trend is observed for which the wear rate decreases with increasing hardness. Although the response is monotonic, the stainless steel pin produces an outstanding amount of wear, about six times as much as any of the others.

Although the result with stainless steel may at first be a paradox, the wear dependence of composites on pin hardness may be explained using the illustration of Figure 4. For materials with hardness values approaching, or greater than those for the reinforcing filler, the matrix and filler wear slowly together and a polishing effect is obtained as observed from our post wear microdefect analysis. With sufficiently soft materials; but presumably harder than the matrix, the rough edges of the filler wear the pin, and the resulting rough edges of the pin penetrate and preferentially wear the matrix. Eventually essentially unworn filler particles are dislodged and washed away with the wear debris. It is conceivable that some filler particles are lodged in the surface of the pin and thus produce accelerated wear on the composite. The microdefect analyses described later in this report substantiates the validity of this mechanism.

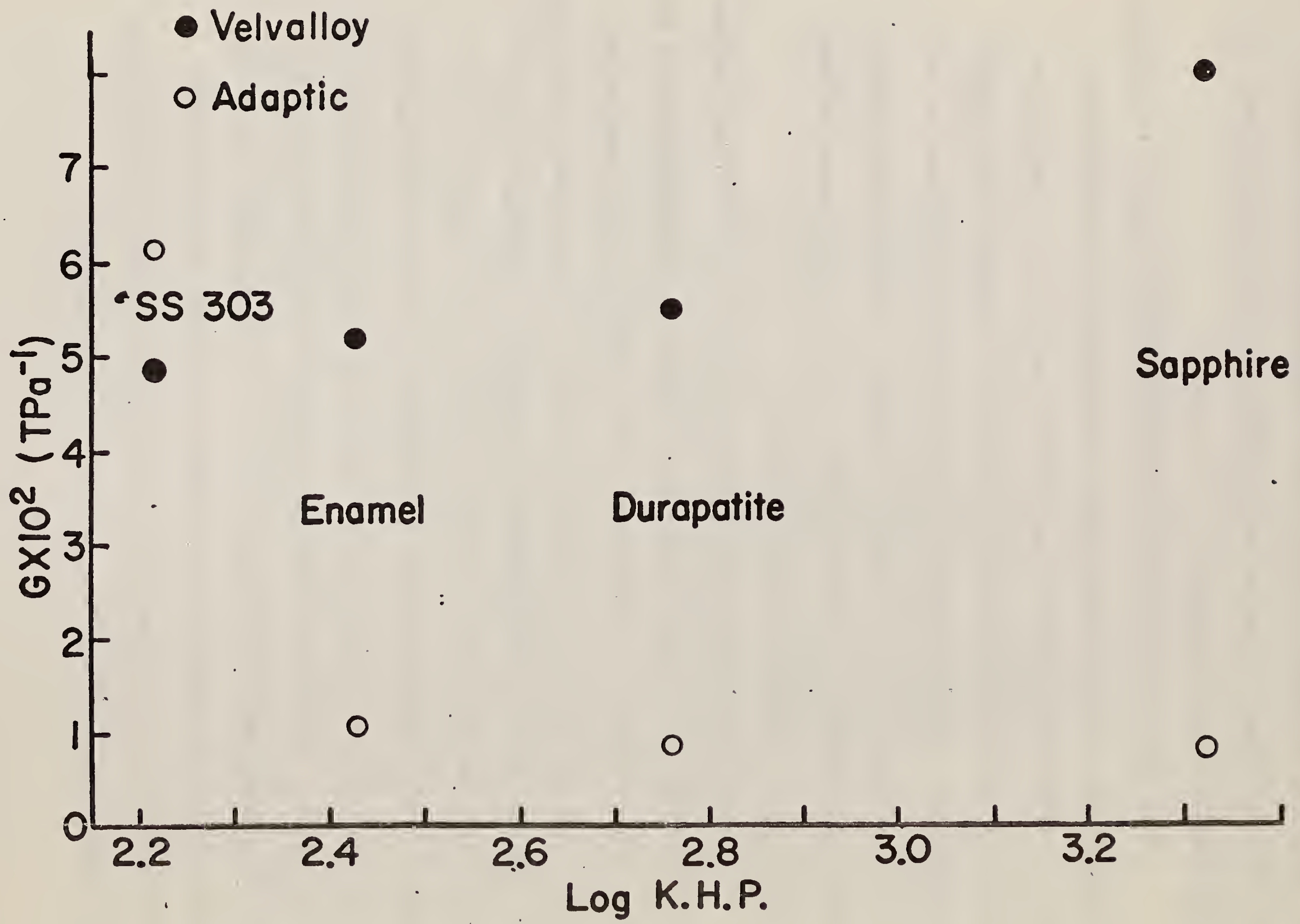

Fig. 3. Wear rates of Velvalloy and Adaptic plotted against Knoop Hardness Number.

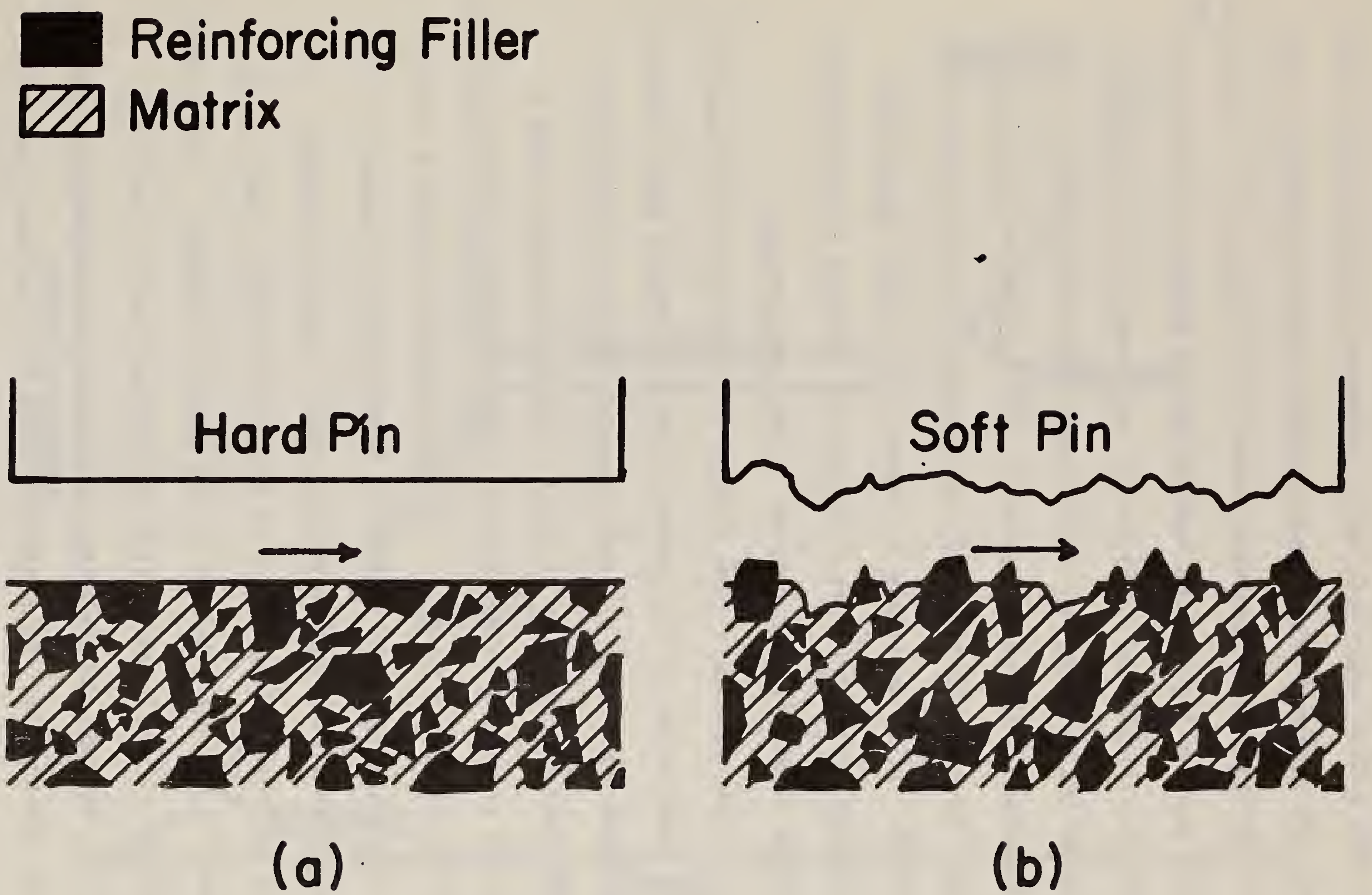

Fig. 4. Schematic drawing illustrating the reason for increased wear of dental composites with a softer wear pin.

In a previous annual report [1] we stated that we observed a low initial wear for Velvalloy using a stainless steel pin. The initial transient with a small wear rate and a subsequent steady state of much higher rate are repeated after a sufficiently long rest period. This behavior is believed to be somewhat general for alloys and is attributed to a passive surface layer which reforms during dormant periods [8]. Accordingly, as illustrated in Figure 5, the formation of the passive layer leads to two wear regimes called oxide and metallic wear. Presumably, the wear in the oxide region is less because of the reduction of adhesion. As shown in Figure 5, the process is repeated after a dormant period. It is desirable to repeat this process because the initial response during the first time may be obscured from "break in" scatter, which is usually encountered in wear measurements.

In order to obtain some insight into the nature of composition change with penetration of the surface, some preliminary Auger spectroscopy measurements were made on several dental alloys in collaboration with the NBS Surface Chemistry Division. Observations were made on Velvalloy; the crown and bridge alloys, Ticon, Ceramalloy and Pentillium; and nickel was used as a control. All measurements revealed a decrease in oxygen concentration with sputtering time which is a measure of the depth penetration of the sputtering ions and of material removed. In addition to the observed depletion of oxygen with depth, some changes were observed in the distribution of the metallic elements. For example, with Velvalloy, silver appears below the surface, but is completely absent at the surface. On the other hand there is a decrease in tin content with penetration. At present we have only two measurements on each material mentioned above:

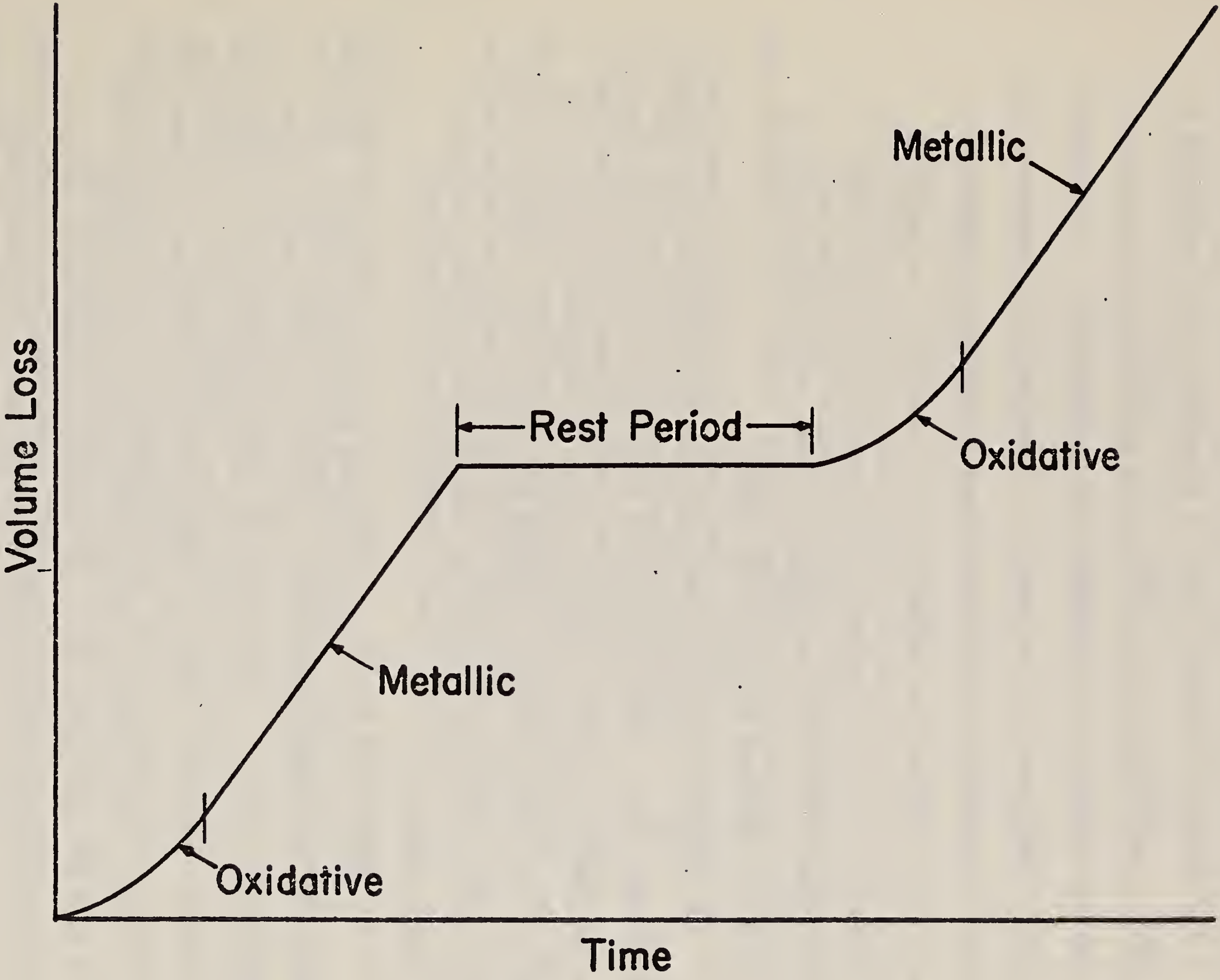

Fig. 5. Typical wear response of alloys illustrating initial transients of low wear following rest periods.

one initial (without sputtering) and one after sputtering with Argon ions for ten minutes, which is estimated to remove 100 Å of material. We intend to obtain more extensive depth profiles on dental alloys in the next year.

The behavior described above is expected to have relevance to in vivo wear. Mastication occurs over short periods with long rests in between (except possibly in cases where bruxism persists). Consequently, it is doubtful that the passive surface is ever completely removed, which would result in very little wear as observed for amalgams. Finally, we point out that if the initial value of $G = 0.0019\ TPa^{-1}$ for Velvalloy (with stainless steel pin) instead of its steady state value 0.0488 (Table 22) along with 0.0615 for Adaptic, a very strong correlation (a factor of 32) is obtained with clinical tests.

Pin and disc wear tests were made on the three crown and bridge alloys mentioned above. These alloys are being evaluated in collaboration with the base metal-porcelain interface activity described in Part IV of this report. On these materials sapphire pins were used. Attempts to use durapatite were unsuccessful because of repeated pin fracture when worn against these materials.

The results for the crown and bridge alloys are given in Table 23. The meanings of the standard deviations σ_1 and σ_2 are the same as those included in Table 22. t_0 is the extent of the transient time over which low initial wear is observed. There are essentially no differences between the low wear rates of these materials which approximate that for Adaptic worn against a hard pin (see Table 22). Of the three Ceramalloy is the only one which did not exhibit any initial transient wear. This may result from the presence of boron in this alloy (which is apparently not present in the others.)

TABLE 23

Wear of Crown and Bridge Materials And Microfilled Composite Using Sapphire Wear Pins

Material	G TPa^{-1}	σ_1 TPa^{-1}	σ_2 TPa^{-1}	t hrs
Ticon	0.0064	0.00076	0.0012	4
Ceramalloy	0.00770	0.000054	0.00037	0
Pentillium	0.0062	0.000050	0.0022	2
Profile	0.043	0.000088	0.016	-

The results for a Strontium glass filled composite Profile are also included in the table. Profile wears much faster than the conventional composite Adaptic and approaches that for the amalgam (see Table 22). Note that according to the standard deviations, σ_1 and σ_2, the wear is very smooth with time; however, the sample is quite inhomogeneous. We plan to obtain wear data on Profile using stainless steel wear pins for the reason mentioned earlier with respect to influence of pin hardness.

According to the microdefect analysis using a silver staining technique described later in this section, *in vivo* worn composite specimens show considerable subsurface damage. *In vitro* worn specimens show considerable damage using stainless steel pins at 10 MPa. In order to determine the influence of stress on damage, pin and disc wear measurements were made on Adaptic specimens at six different stress levels using stainless steel pins.

During these experiments we obtained a trend in the wear rate which we have not noticed before. The wear proceeds at constant rate (with time) over a certain region and then increases by roughly a factor of two and then continues at the larger constant rate indefinitely. Examples are illustrated by Figure 6, where the track depth is plotted against time at 5 and 12.5 MPa normal stress. The damage accumulated during the first region is believed to cause the change of rate at the onset of the second region. Similar behavior is observed by Dowson [9] and coworkers at the University of Leeds on high molecular weight polyethylene. They attribute the first region to an adhesive mechanism and the second, adhesive plus fatigue.

The wear rates (G_1 and G_2) for the two different regions for Adaptic are summarized in Table 24 along with their ratio. The stress dependence of the wear rates appears to be somewhat constant at the low stresses (except at 2.5 MPa where no significant wear is observed) and then increase rapidly with increasing stress. From the microdefect analysis the qualitative damage rankings (with increasing damage) are given on the right. Damage appears to increase with increasing stress to about 10 MPa and then gradually decreases. We believe that the reason for the decrease in the observed damage above 10 MPa is that the wear there is more severe, hence damage layers are removed as wear progresses.

No damage is apparent on Adaptic specimens when wear is terminated within the first region (using stainless steel pins) or at anytime when enamel, or enamel like, pins are used. We have also not observed the changes in the wear rate as described above when enamel, or enamel like, pins are used. Since *in vivo* worn specimens reveal subsurface damage, these results preclude the possibility of using enamel, or enamel like, wear pins to simulate *in vivo* wear.

Pin and disc wear measurements were also made on Adaptic specimens immersed in certain chemicals as part of a study described later in this section.

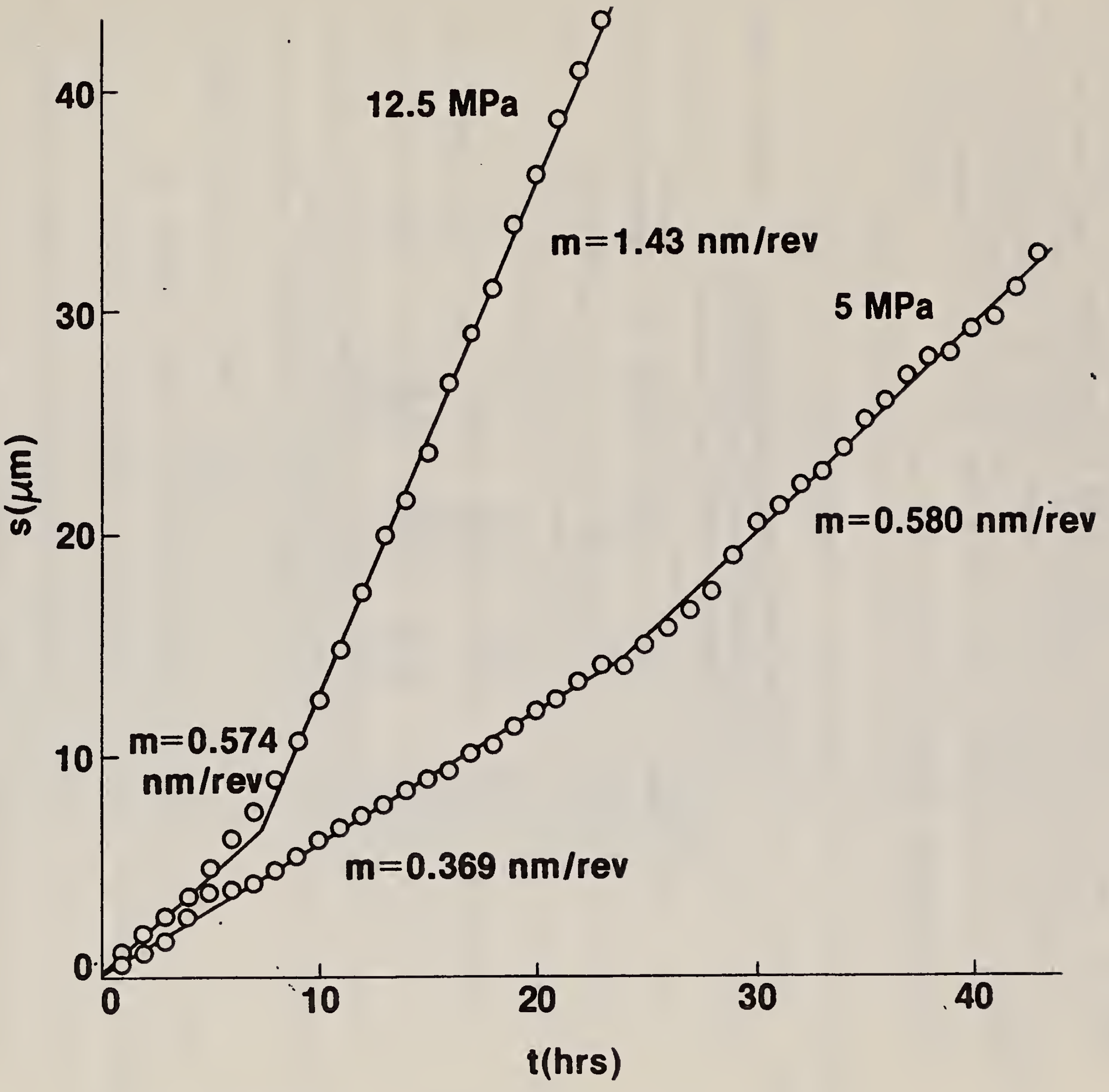

Fig. 6. Track depth versus time curve for Adaptic at a stress level of 5 and 12.5 MPa revealing two regions of different wear rates.

Of the specimens stored in ethanol, cyclohexanol, and distilled water for two weeks at 37°C, only the last revealed no damage. Wear measurements on the others showed up to 90 μm of material removed over the first revolution in contrast to the water immersed specimen for which no material loss was observed. From there on the steady state wear rates are essentially the same. It is apparent that the damage resulting from ethanol and cyclohexanol is so severe that the wear resistance of the inflicted damage regions is essentially null.

Table 24

Wear Measurements on Adaptic
At Different Normal Stresses Using
Stainless Steel Wear Pins

Stress MPa	G_1 TPa	G_2 TPa	G_2/G_1	Damage Ranking
2.5	0	0		0
5.0	0.37	0.58	1.57	1
10.0		0.92		3
12.5	0.57	1.43	2.49	2
15.0	1.91	5.10	1.46	1
20.0	6.5	7.4	1.14	0

B. Subsurface Damage Analysis Investigations

A staining technique was developed to reveal the micro-defects inside dental composites, specifically in the damage zone immediately beneath the worn surface. Fine silver particles were introduced into the defect region and the extent of damage, e.g. development of microdefects, was examined qualitatively with optical microscopy and quantitatively with microprobe technique.

1. Analysis Applied to Clinically Worn Composite Materials

Fifteen in vivo worn dental composites and two unfilled plastic (PMMA) components from a clinically worn partial denture were examined. These clinically worn specimens were provided through Dr. Everett Cobb, a guest worker on the staff from the Georgetown University Dental School. The results of the examination of these specimens are summarized as follows:

(1) Only few crazes or microcracks were observed at the wear surface of the PMMA denture teeth. These cracks are found to be perpendicular to the wear surface. No severe damaged zone was found. However, it is noteworthy that this observation was made on two samples (molar) from a partial denture, consequently, the force exerted on these pieces may not be as great as that on a normal tooth.

(2) Damage layers of 10 µm to 200 µm were observed on occlusal surfaces of the dental composites, on the mesial surfaces covered with plaque and around internal air bulbs opened to the wear surface. (e.g. see Fig. 7)

(3) The thickness of the damage layers varied from location to location; whereas the damage zones around the air bulbs opened to the wear surface had rather uniform thickness.

(4) Within the damage layers, the silver seemed to collect preferably around the filler particles, especially around the larger ones.

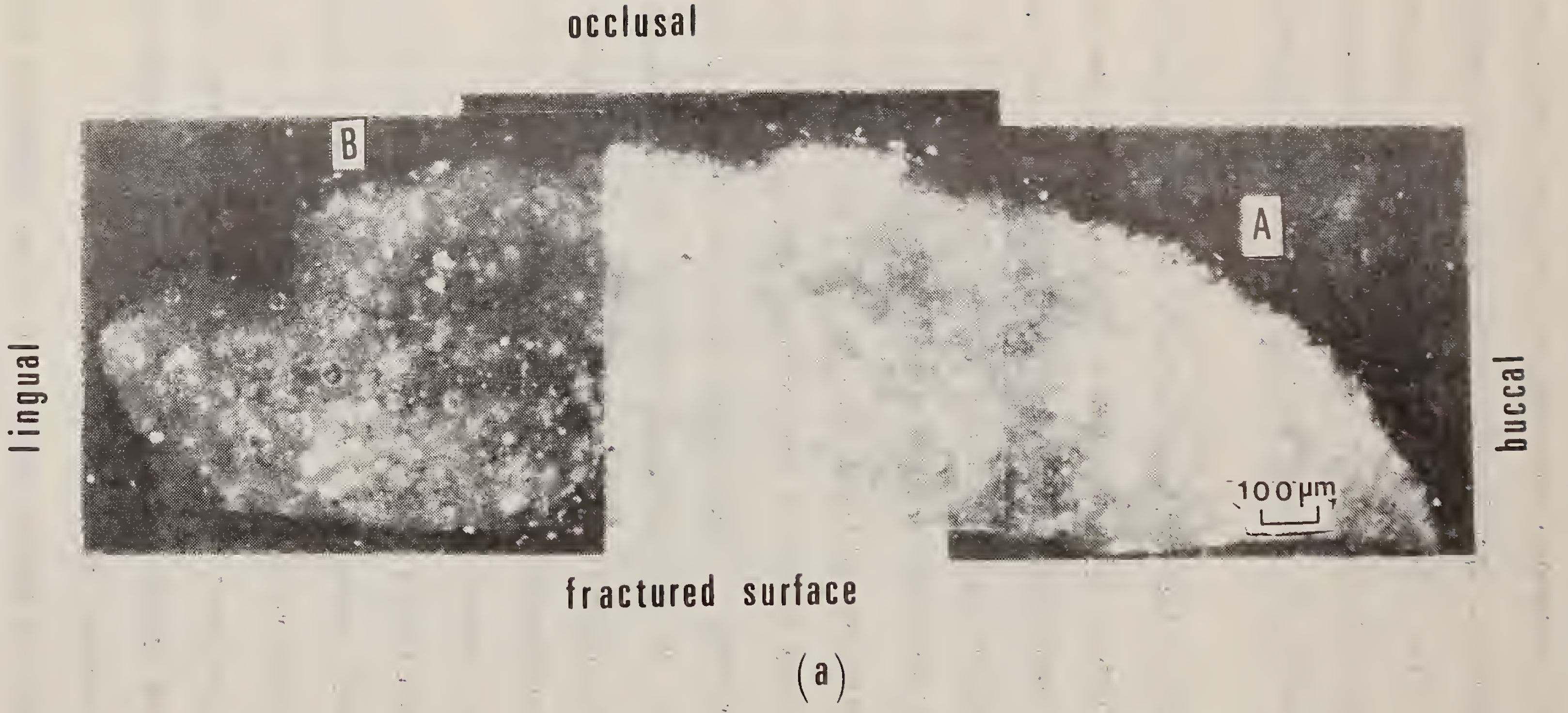

Fig. 7. A longitudinal section of a clinically worn dental restorative composite, the subsurface damage beneath the occlusal surface becomes visible after silver staining.

(5) The wear surfaces of the in vivo worn composites were not smooth; filler particles protrude on the wear surface.

(6) The quantity of silver vs. the depth of the damage layer was measured with microprobe using the copper L_α line. The result indicated a rather sharp boundary exists between the damage layer and the undeformed part.

The above observations tend to suggest that the in vivo wear process in dental composites is a combination of chemical and mechanical erosion, preferably occurring at the particle-matrix interface.

2. Analysis Applied to In Vitro Worn Composite Materials

Employing the silver staining technique to examine in vitro worn composite restoratives indicated that:

(1) No damaged sublayer was observed beneath an Adaptic sample worn by a durapatite pin in a pin and disc wear test. The normal load used in this test was 10 MPa. Furthermore, the filler particles were found to be worn away at the same rate as for the matrix. Consequently, the wear surface was smooth without any protruding particles.

(2) Five in vitro worn Adaptic samples obtained from the same pin and disc wear equipment but with a stainless steel pin were examined. The normal loads applied on these samples were 5, 10, 12.5, 15 and 20 MPa, respectively. Protruding filler particles were found on the wear surface of all samples. Maximum sublayer damage was observed on samples worn with 10 MPa normal load; little sublayer damage was observed when the load is increased to 20 MPa force.

(3) No sublayer damage could be observed on the thermal-cycled composites that were not exposed to a physical wear process. The dental

composite samples were prepared with Concise material following the procedure recommended by the manufacturer. Samples had been aged in 37°C water for 2 weeks prior to the thermal cycling test. During the cycling test, the composites were immersed in the 5°C and 55°C water baths alternatively and the dwell time in each bath was 75 seconds. Samples were removed after completing 3800 cycles and 7600 cycles and subjected to the silver staining technique.

(4) No sublayer damage was observed within acid immersed composites. The samples used were identical to those for the thermal cycling tests. Lactic acid, formic acid and acetic acid were chosen for the etch test. The solution pH was maintained at 4.5 throughout the test. Composite samples were stored in the solutions at 37°C for one and two weeks before they were removed. No change in structure of these acid treated composites could be detected using the silver staining technique. These specimens were not subjected to any physical wear process.

(5) Some minor amount of filler and matrix interfacial damage was observed in compression fatigued dental composites. The samples were again prepared in an identical way as those for the thermal cycling or acid tes. A servo-control MTS equipment was used for the compression fatigue test. For Concise material the fatigue limit has been previously determined to be approximately 145 MPa for 5,000 cycles [10]. Throughout the present work, the load was cycled between 0 MPa and 145 MPa. Samples were obtained after 500, 1000, 2000, 4000 and 8000 cycles. Subsurface defects, mainly along the filler and matrix interface, were observed using the silver staining technique. However, the extent of damage caused by compression fatigue appears to be much less compared with that observed among clinically worn samples that were examined in the same manner.

3. Analysis Applied to Thermal Cycled, Acid Immersed or Compression Fatigues Composite Specimens

Change in mechanical properties of these samples subjected to thermal cycling, acid etching and compression fatigue was monitored by Knoop microhardness tests. The results are listed in Table 25, and the data presented are an average of ten measurements. These microhardness test results suggest that (1) thermal cycling between 5°C and 55°C does not degrade the physical properties of the composites. In fact, the hardness seems to increase as a result of the thermal cycling. This may be caused by further polymerization of BIS-GMA in the 55°C environment. (2) Except with lactic acid, no deterioration in mechanical property as revealed by hardness was introduced by the organic acid treatments. Verification of the lactic acid results is being sought. (3) Although certain minor amounts of filler-matrix interfacial defect was introduced through the compression fatigue test, the structure damage caused by fatigue is apparently not enough to cause any decrease in hardness.

4. Analysis Applied to Organic Solvent Immersed Composite Specimens

Eight chemicals with solubility parameter δ ranging from 7.4 to 14.7 $(cal/cm^3)^{1/2}$ were chosen to study their effects on the mechanical strength and the structure of BIS-GMA based polymer. Water was used as the control for this study. One commercial dental restorative composite (Concise) and one unfilled BIS-GMA (70)/TEGDMA (30) resin were immersed in these chemicals. Changes in sample weight and surface hardness were monitored with time.

No significant change in sample weight was observed over the test period of four weeks, e.g. the data of weight change of Concise

Table 25

Knoop Microhardness Test Results of Dental Composites (Concise)

Sample Specification	Average	Standard Deviation
Compressive fatigue 144 MPa/8000 cycles	57.5	2.82
Thermal cycled 5°C-55°C/7600	75.4	3.42
Thermal cycled 5°C-55°C/3800 cycles	59.4	3.03
Lactic acid, pH = 4.5 2 weeks	48.4	3.14
Acetic acid, pH = 4.5 2 weeks	74.1	3.02
Formic acid, pH = 4.5 2 weeks	69.4	3.37
Control	55.2	3.53
Control	56.04	7.25
Control	58.8	1.46

is given in Figure 8. However, dramatic decrease in hardness (KNH) was observed in both Concise and the unfilled resin. After these materials were immersed in chemicals with solubility parameters ranged from 8.9 to 14.7 (Figure 9 and 10). The decrease in hardness is quite severe, e.g. in unfilled BIS-GMA resin more than 70% of the original hardness was lost over a period of three weeks. For samples immersed in heptane ($\delta = 7.4$) and water ($\delta = 23.4$), the hardness either increased or remained constant.

The structure of the chemical-immersed BIS-GMA composites was examined by the silver staining technique. A defect layer was observed in all the samples suffering a reduction in hardness. The resultant structure of a composite after immersion in ehtanol is shown in Figure 11 which is rather similar to that observed within the clinically worn samples.

This work establishes the fact that BIS-GMA based polymers or composites are susceptible to deterioration by various chemicals.

Initial wear test data from this laboratory's pin-on-disc machine was obtained on samples immersed in ethanol, cyclohexanone and water and is reported in Section III A of this report.

C. Three-Body Wear Test

The purpose of this effort is to explore the role of three-body wear as one of or perhaps the dominant mechanism in the *in vivo* wear process. The hypothesis here is that the wear medium in the oral environment is essentially food particles or debris instead of the opposing tooth, and that the wear mechanism involves a chemically accelerated erosion process instead of rigid surface contact abrasive wear.

In this approach, aqueous polyvinylalcohol (PVA) solution of various viscosity were chosen to simulate the action of food particles.

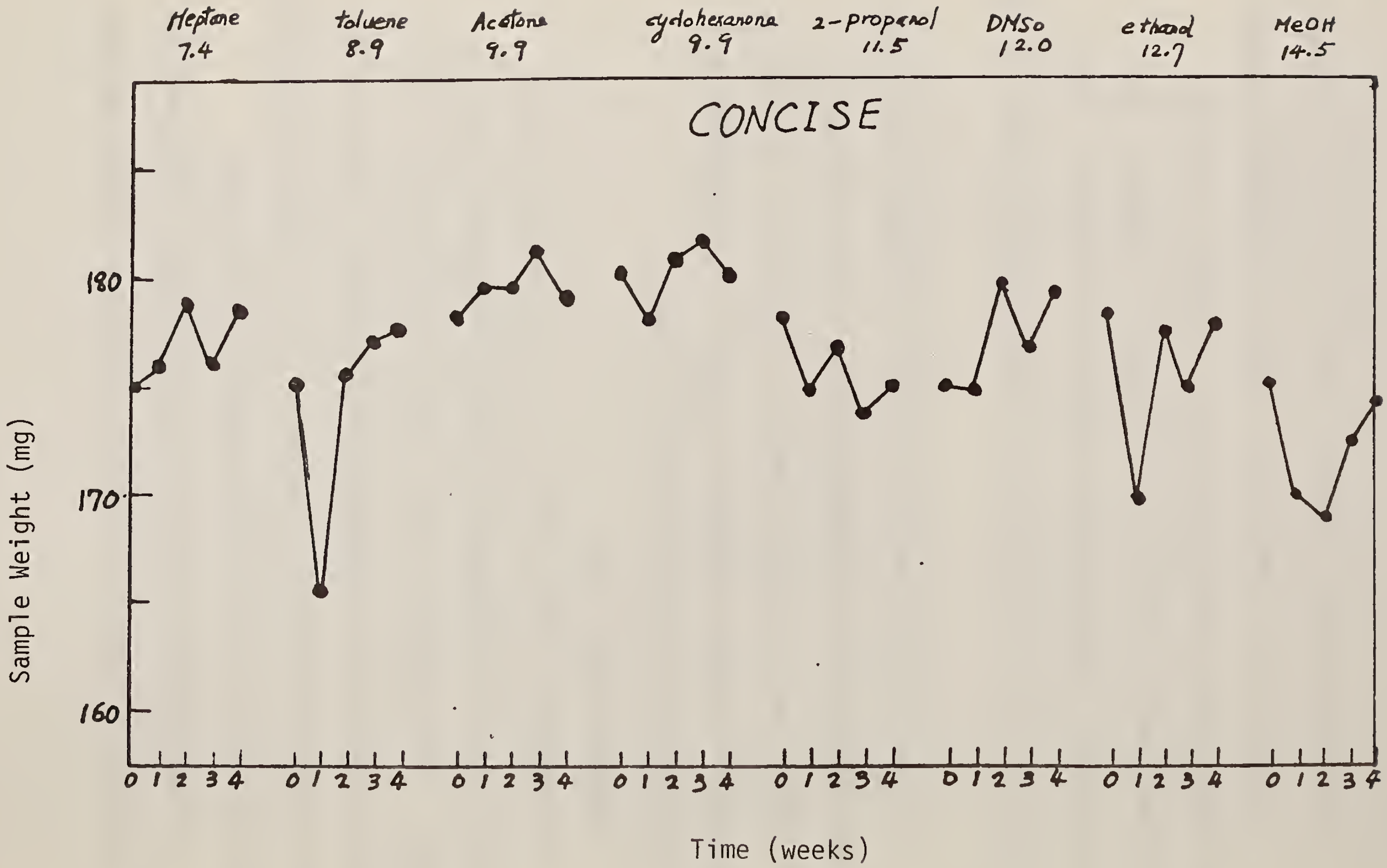

Fig. 8. Change in weight of samples immersed in chemicals of different solubility parameters.

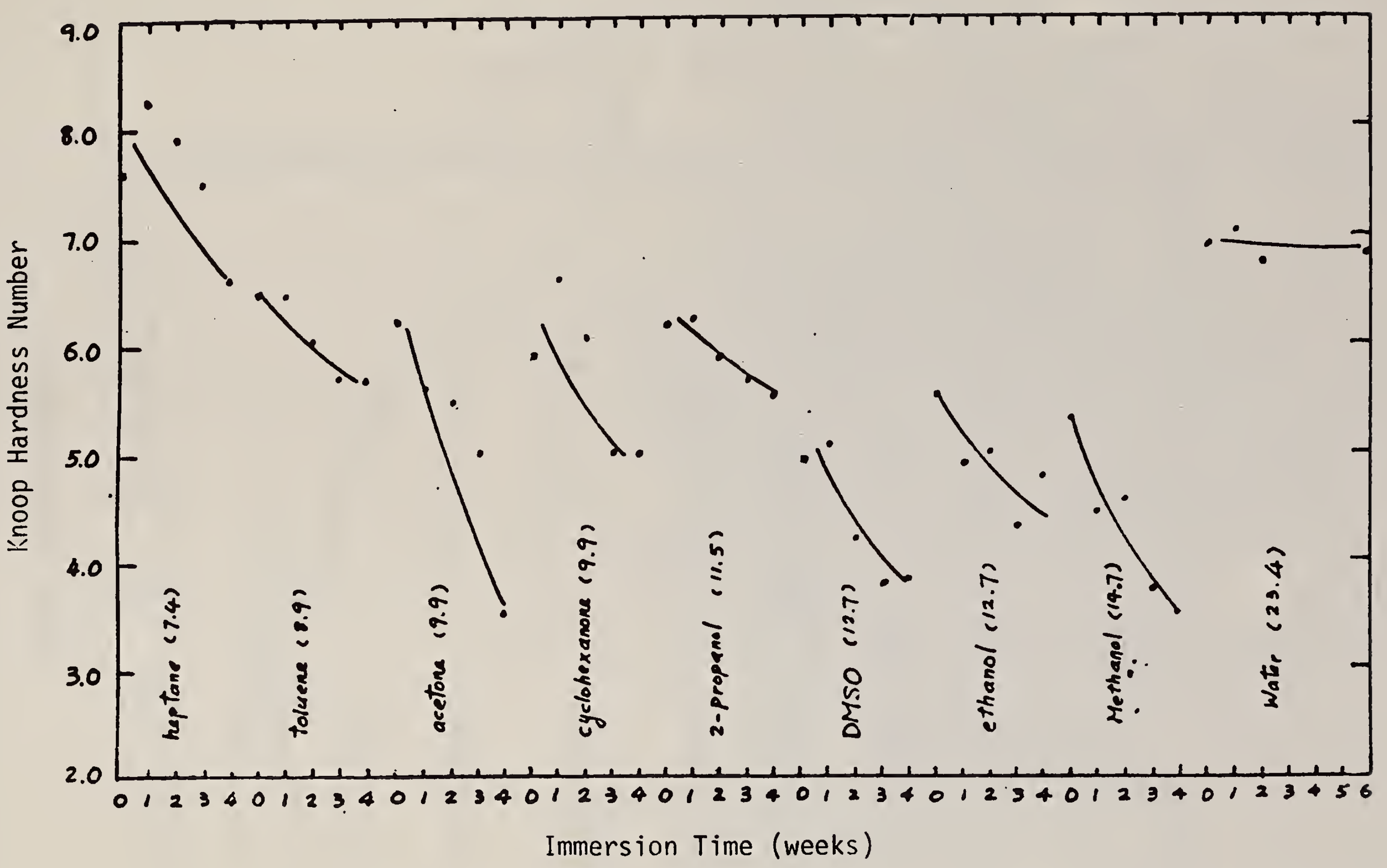

Fig. 9. Effect of chemicals with different solubility parameters or Hardness of a dental restorative composite (Concise)

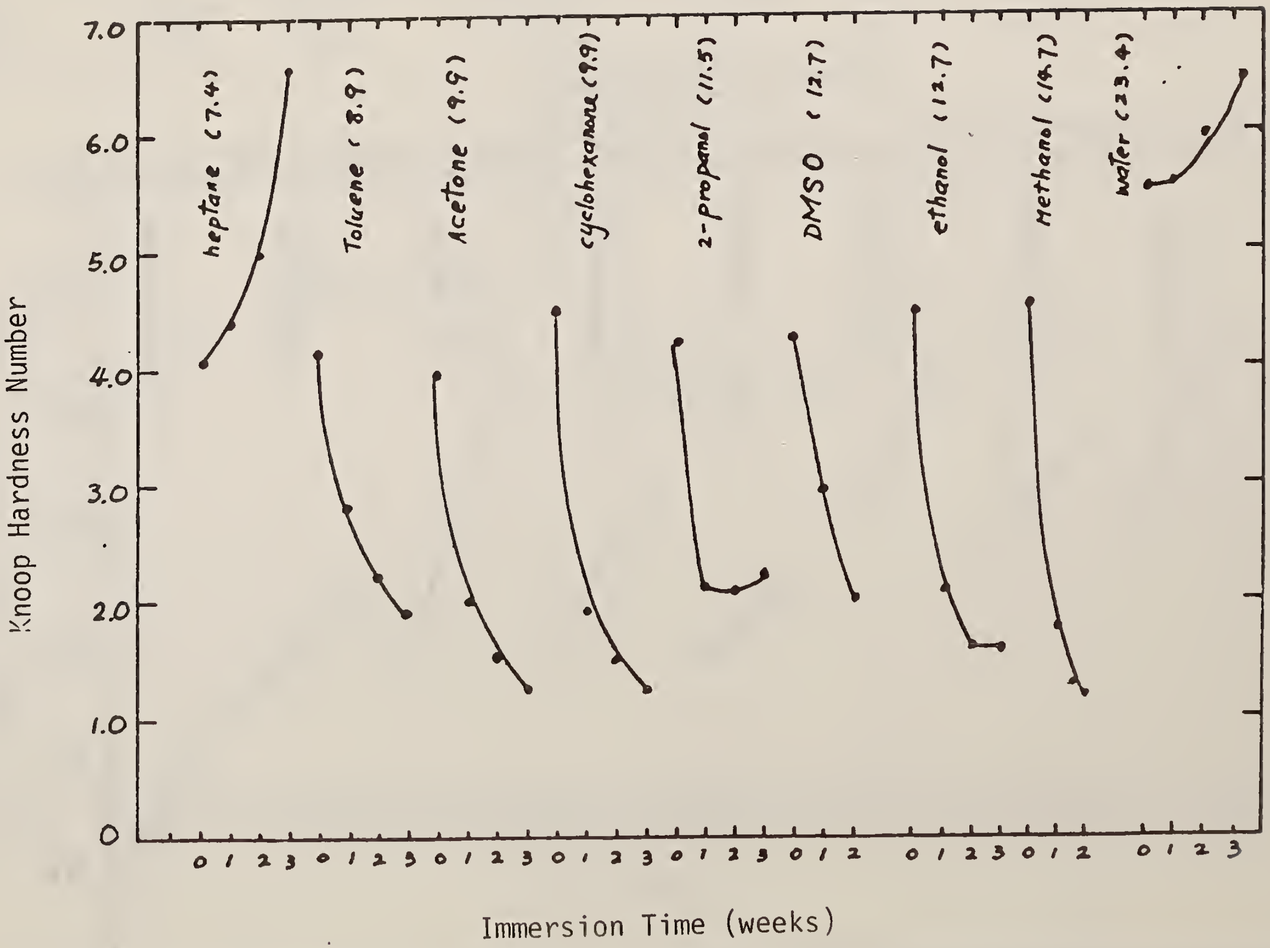

Fig. 10. Effect of chemicals of different solubility parameters on Hardness of unfilled BIS-GMA (30% TEGDMA) polymer.

Fig. 11. Section of a dental restorative composite (Concise) after softening by ethanol. The damaged layer becomes visible after being silver stained.

The wear samples are dental composites and dental amalgam placed in extracted teeth which are in turn mounted in a fixing medium in such a manner that two amalgam and two composite specimens are simultaneously subjected to the viscous medium which distributes a selected load to the specimen surfaces in a manner simulating food particles between occlusal surfaces. A confining cell for the PVA and the specimens has been designed and assembled to operate with hydraulic-servo testing equipment. The experimental variables to be examined are the viscosity of the wear medium, influence of abrasive particles, and influence of chemicals with known solubility parameters.

IV. Dental Alloys, Ceramics and Implants

Lower initial cost and often superior properties have rendered nonprecious alloys as an increasingly attractive option to the use of gold alloys in fixed partial dentures, both with and without porcelain veneers. Previous reports [1,2] addressed the problem of achieving clinically acceptable fits with single unit castings and the ability of porcelain powders to "wet" [11] nonprecious alloy surfaces, thereby leading to potentially strong chemical bonding between procelain and alloy.

Current studies of porcelain/alloy compatibility are directed toward defining the properties of porcelains and alloys as they relate in terms of residual stress for veneered prostheses. It is anticipated that clinicians, laboratory technicians and industrial personnel will be able to use such information toward defining porcelain alloy combinations which will best achieve the desired end results in function.

Additional studies are in progress regarding fit and castability of nonprecious and "semi-precious" dental alloys. Objectives include development of practical tests for evaluation or ranking of castability and for refining/defining techniques for production of clinically acceptable multiple unit fixed partial dentures. Although the technique for producing well fitting single unit castings has been described [12], there is no assurance that said technique will produce the desired results with multiple unit castings.

Peripherial studies in dental ceramics involve fluorescence in dental porcelain and manufacturing of feldspathic frits. Manufacturers are introducing porcelain products which utilize fluorescing agents other than undesirable uranium oxide. If satisfactory fluorescence quality is achieved in these products it may not be necessary to continue said studies, however, this remains to be determined. Regarding manufacturing of porcelain from feldspar, the high quality, low ion feldspars are becoming more difficult to procure, hence, new sources and/or methods of producing porcelains are desirable.

Finally, areas of activity which were being pursued at the start of FY80 included (1) calculation on the secondary radiation dose delivered to local oral tissues following neutron irradiation of gold prostheses and, (2) the start of finite element modeling studies of stress in tissue around healthy and periodontially involved teeth, using refined non-linear discrete fiber modeling of the periodontal membrane. The radiation study was brought to conclusion before final recommendations were made by NIDR to focus on the ceramic/alloy area. The second study was brought to the point that development of a finite element tooth model had been made, at which time, further activity with NIDR support was terminated.

A. Poreclain-Alloy Characterization

1. Thermal Expansion

Characterization of porcelain materials used in veneering of dental alloys has progressed to the point that the thermal expansion of all materials currently of interest has been determined at least once. In Fig. 12 the thermal expansion of opaque porcelains, fired from either 1 to 7 times is shown. Similar results are presented in Fig. 13 for body porcelains. At this time, without additional determinations for several of the porcelain firings, systematic trends in expansion with number of firing cycles are not apparent except for Microbond

Opaque and Vita VMK-68 body porcelains. Table 26 lists the same data along with the expansion values of a number of precious and nonprecious alloys. The significant feature that may be derived from these data is the large difference in thermal expansion which exists between the lower expanding alloys and the higher expanding porcelains and, between the higher expanding alloys and the lower expanding porcelains. The differences can be seen to approach 30%. As Neilson and Tuccillo [13] had concluded that ∿7% mismatch in thermal expansion is the most which can be safely tolerated, it is clear that not all porcelain/alloy combinations can be expected to provide an unequivocal prognosis for successful use; in fact some must fail if thermal expansions were the only factors determining success. As will be shown further in experimental/theoretical studies of composite split rings, other factors must enter into operation which no doubt "save" what could be otherwise unacceptable combinations.

2. Compatibility Index

Another important result of the thermal expansion studies lies in the relatively large differences in excess volume which are trapped in porcelains cooled according to manufacturers recommendations for fabrication of dental crowns. These differences are depicted in Figs. 14 & 15. Because of this trapped volume, a correction must be applied to the compatibility index proposed by Ringle [14], et al, and modified by Fairhurst [15]. According to Fairhurst:

$$C_i = K\int_{\circ}^{T_g + b\ln|q|} \left(\alpha_{p,a} - \alpha_A\right)\, dT. \qquad (1)$$

Where C_i is the compatibility index, T_g is the glass transition temperature, b is a constant, characteristic of a given porcelain, q is the absolute cooling rate and $\alpha_{p,a}$ is the thermal expansion coefficient for annealed porcelain and α_A is the thermal expansion coefficient for the alloy. In a paper in review for publication [16], it is shown that as the thermal expansion for rapidly cooled porcelain should be used, a correction Δc must be applied to eq. 1, rendering a corrected compatibility index, $C_{ic} = C_i + \Delta C$ (2)

Δc is shown to be

$$\Delta C = \int_{T_o}^{T_g + b\ln|q|} (\alpha_{pc} - \alpha_{pA})\,dT \qquad (3)$$

where α_{pc} is the thermal expansion coefficient for rapidly cooled porcelain and $\alpha_{p,A}$ is the value for annealed porcelain.

From Figure 16:

$$\Delta c = \left(\frac{\Delta \ell}{\ell}\right)_{T_o,\,\substack{\text{fast}\\\text{cool}}} - \left(\frac{\Delta \ell}{\ell}\right)_{T_o,\,\substack{\text{slow}\\\text{cool}}} \qquad (3a)$$

and hence is related to the excess volume, ΔV, recovered,

$$\Delta C \approx 3\Delta V \qquad (4)$$

3. Porcelain/Alloy Split Ring Studies

The advantages of using a porcelain veneered split metal ring for compatibility studies were presented at the 1980 AADR meeting in Los Angeles [17]. In such studies, the change in gap is taken as a measure of compatibility, with zero change assumed to be associated with a state of minimum overall residual stress within the system. Features which suggest the split ring may be a reasonable indication of compatibility are 1) the self referencing feature of gap measurements, 2) curvilinear geometry which results in generation of radial as well as tangential stress, 3) dimensions which produce curvature such that stresses generated should be of similar magnitude to those generated in a crown,

4) geometry such that cooling of a crown is reasonably approximated by cooling of the split ring, i.e. a porcelain veneer of typical restoration thickness; porcelain on one side, metal on the inner side; cooling from edges somewhat as might be experienced around margins, 5) gap opening or closing should be indicative of opening or closing of margins.

In order to develop a balanced study, both experimental and theoretical approaches are being pursued, with the objective of fine tuning the theoretical studies via use of measured material properties so that theory and experiment are brought into the closest agreement possible. As detailed information on stress in multilayered systems should develop from the theoretical studies, the hypothesis of using a split ring for a compatibility test can be reviewed critically.

At the time of this report four porcelain/split ring systems have been fired experimentally according to porcelain and alloy manufacturers' instructions. Three specimens of each system were tested. The porcelains evaluated were Ceramco[a], Vita-VMK-68[b], Biobond[c], and Will-Ceram[d], the metal alloy ring in each case was Pentillium[e]. Each series was fired vs a control ring without porcelain. The total firing sequence consisted of conditioning the alloy, applying opaque and firing, applying body and firing and then firing through a natural glazing cycle. Experimental results of the net change in gap are shown in Figure 17. Generally, the precision is ∿2-3% except for the Will-Ceram/Pentillium system. The larger standard deviation of ∿10% could indicate that this particular combination of porcelain and alloy may lead to less-consistency

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[a] Johnson & Johnson Co., E. Windsor, NY
[b] Vita Zahnfabrik
[c] Dentsply International, York, PA
[d] Williams Gold, Buffalo, NY
[e] Pentron Corp., Wallingford, CT

during fabrication in the dental laboratory.

Theoretical calculations of the change in gap for Ceramco or Vita-VMK-68 on Pentillium alloy yield changes several times greater than the experimentally observed values. This indicates that stress relief is occurring in the porcelain at temperatures well below the glass transition temperature. This also leads to further need to use the compatibility index (which currently has no allowance for viscous flow) with caution in interpreting or predicting compatibility test results.

Finally, the stress system used in the compatibility index appears rather over simplified, although there is often great merit in simplicity. Shown in Figure 18 is a schematic representation of bi-material stress as derived from the Timoshenko analysis (developed to predict strain using simplified stress analysis). In such a representation, no shear stresses can be calculated, although shear must clearly be present due to the stress discontinuity at the interface. Also, no radial stresses are developed in the case shown. As viscous flow must be responsible for relief of some stress in porcelain, shear stress is an important parameter, and should not be ignored.

B. Dental Alloy Castability

During the past year, a practical castability test has been used to rank the castability of numerous alloys. The test, originally designed by Eden and Dickson [18] of this laboratory, was modified by Whitlock, also of this laboratory, to reduce the standard deviation of test results. Essentially, a rectangular 10 x 10 segment polyester sieve screen of 18 gage is connected to a sprue at one corner with 10 gage runner bars extending along two sides of the mesh. The test pattern is invested, burned out and then cast with an alloy, using the manufacturers' instructions. After devesting, the number of complete segments which are cast is recorded and the percent used to indicate castability. An advantage of the test is that it can be used in any dental laboratory to rank the castability of new alloys vs ones with which the laboratory is familiar. Evaluations are still in progress, however, several nonprecious alloys demonstrate the ability to be cast as well as some previous metal alloys. An abstract has been prepared on this topic, for submission for the 1981 AADR meeting. Further modifications of the test are also being evaluated. These modifications may render the test more sensitive to processing variables, thereby lending the test for use as a qualtiy control procedure to evaluate optimum technique in laboratories.

An ancillary program of casting evaluation was initiated to investigate how well multiple unit fixed partial denture castings fit under the conditions shown by Eden [12] to produce the optimum fit for single unit castings. Early results show clinically unacceptable fits for multiple units, even though single units sectioned from the bridges, fit well.

C. Radiation Dose from Neutron Activated Dental Materials

A paper was presented at the AACR meeting in Los Angeles in 1980 [19]. This paper has been refined for publication and is currently under review at NBS,

Conclusions are that high levels of β-plus γ radiation can be delivered to local tissues following exposure to 50 REM of thermal neutrons. For gold the dose is 30 REM, $\beta + \gamma$. Silver, cobalt and indium also have high thermal neutron cross sections and these, too, would be expected to produce substantial secondary doses in basal cells following activation by sub-lethal neutron doses, e.g. 50 REM.

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Invited Talks

New Monomers for Use in Dentistry. J. M. Antonucci, American Chemical Society Meeting, Houston, Texas.

The Accelerative and Adhesive Bonding Capabilities of Surface Active Accelerators. J. M. Antonucci, 58th Annual Meeting IADR, Osaka, Japan.

Initiator-Accelerator Systems for Acrylic Resins and Composites. G. M. Brauer. American Chemical Society Meeting, Houston, Texas.

Derivatives of p-N,N-Dialkylaminophenylalkanoic Acid: New Accelerators for Dental Composites. G. M. Brauer. 58th Annual Meeting, IADR, Osaka, Japan.

Dental Alloy and Ceramic Compatibility. J. A. Tesk. International Precious Metals Institute, Toronto, Canada.

Wear Mechanisms of Dental Composites. Wen-li Wu. Johnson & Johnson, East Windsor, NJ.

Structure and Stress of Cross-linked Polymers During Polymerization. Wen-li Wu. Gordon Research Conference, New London, NH.

Plastic Deformation of Doubly Oriented Crystalline Polymers. Wen-li Wu, University of Massachusetts, Amherst, MA.

Abstracts (AADR, Los Angeles, March, 1980) on Microfilm

Biocompatible Amine Polymerization Accelerators: *Para*-Dimethylaminobenzoic Acid and its Ethyl Ester. Abstract 291, J. M. Antonucci, R. J. Peckoo, C. Schruhl and E. E. Toth.

In Vitro Wear Measurements on Dental Materials. Abstract 327, J. E. McKinney.

Intraoral Secondary Radiation Dose from Neutron Activated Dental Materials. Abstract 326, J. A. Tesk and R. P. Whitlock .

A Porcelain Veneered Split Metal Ring for Evaluation of Compatibility of Dental Porcelain-Alloy Systems. Abstract 660, R. P. Whitlock[1], J. A. Tesk E. E. Parry[1] and G. E. O. Widera[2]

Theoretical Stress Analysis of Porcelain Veneered Split Metal Ring for Evaluation of Compatibility of Porcelain-Alloy System. Abstract 652, G. E. O. Widera[2], J. A. Tesk and R. P. Whitlock[1]

Abstracts (IADR, Osaka, Japan, June 1980) on Microfilm

The Accelerative and Adhesive Bonding Capabilities of Surface-Active Accelerators. Abstract 195, J. M. Antonucci, D. N. Misra[3] and R. J. Peckoo.

Derivatives of p-N,N-Dialkylaminophenylaklanoic Acid: New Accelerators for Dental Composites. Abstract 194. G. M. Brauer and J. W. Stansbury.

Observations of Significant Differences in Thermal Expansion Characteristics of Dental Porcelain. Abstract 40, R. P. Whitlock[1], J. A. Tesk, E. E. Parry[1], and G. E. O Widera[2].

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The following manuscripts are under NBS editorial review or have been submitted for publication:

Effect of Diluent Monomer on the Physical Properties of BIS-GMA Based Composites. D. Dulik, R. Bernier and G. M. Brauer.

4-N,N-Dimethylaminophenylethanols, Alkanoic Acids and Esters: New Accelerators for Dental Composites. G. M. Brauer, J. W. Stansbury and J. M. Antonucci.

Biocompatible Amine Polymerization Accelerators: Para-Dimethylaminobenzoic Acid and its Ethyl Ester. J. M. Antonucci, R. J. Peckoo, C. Schruhl and E. E. Toth.

In Vitro Wear Measurements on Dental Materials. J. E. McKinney.

Intraoral Secondary Radiation Dose from Neutron Activated Dental Materials. J. A. Tesk, R. P. Whitlock[1] and A. Holmes.

The Accelerative and Adhesive Bonding Capabilities of Surface-Active Accelerators. J. M. Antonucci, D. N. Misra[2] and R. J. Peckoo.

The Desirability of Using Radiopaque Plastics in Dentistry - A Status Report. G. M. Brauer.

New Monomers for Use in Dentistry. J. M. Antonucci.

Initiator-Accelerator Systems for Acrylic Resins and Composites. G. M. Brauer.

Consideration of Some Factors Influencing Compatibility of Dental Porcelain and Alloys. R. P. Whitlock[1], J. A. Tesk, G. E. O Widera[3], A. Holmes and E. E. Parry .

An Evaluation of the Porcelain/Metal Compatibility Index. J. A. Tesk, R. P. Whitlock[1], G. E. O. Widera[3] and R. W. Hinman[1].

An Amine Accelerator for Color-free Curing of Autopolymerizable Methyl Methacrylate Denture Systems. H. Argentar[2], J. A. Tesk and E. E. Parry[1].

The Porcelain/Metal Compatibility Index and Thermal Expansion/Contraction J. A. Tesk. R. P. Whitlock[1], G. E. O. Widera[3] and R. W. Hinman[1].

Consideration of Some Factors Influencing Compatibility of Dental Porcelains and Alloys; Part I. Characterization. R. P. Whitlock[1], J. A. Tesk, G. E. O. Widera[3], A. Holmes and E. E. Parry[1].

Consideration of Some Factors Influencing Compatibility of Dental Porcelains and Alloys; Part II. Theoretical and Experimental Compatibility. J. A. Tesk, R. P. Whitlock[1], G. E. O. Widera[3], A. Holmes and E. E. Parry[1].

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Abstracts Submitted for IADR/AADR Meeting, March 81, Chicago, IL

Effects of Porcelain/Alloy Interfacial Diffusion Zones on Thermo-mechanical Strain. J. A. Tesk, R. W. Hinman[1], G. E. O. Widera[2], J. M. Cassel, and A. D. Holmes.

Fit of Multiple Unit Fixed Partial Denture Castings. R. W. Hinman[1], J. A. Tesk, E. E. Parry[1].

Cements from 2,5-Dimethoxyphenol and Zinc Oxide. J. W. Stansbury, H. Argentar[3] and G. M. Brauer.

Degree of Polymerization of Dental Resins by Differential Scanning Calorimetry. J. M. Antonucci and E. E. Toth.

Influence of Chemicals on *In Vitro* Wear of Dental Restorative Composites, W. Wu and J. E. McKinney.

Theoretical/Experimental Studies of Stress Compatibility in Porcelain-Veneered Split Metal Rings. G. E. O. Widera[2], J. A. Tesk, R. P. Whitlock[1], R. W. Hinman[1]. E. E. Parry[1].

Application of Silane Coupling Agent to Inorganic Components of Composites. T. M. Chen[4] and G. M. Brauer.

Peroxy Esters and Hydroperoxides as Initiators for Composite Resins. G. M. Brauer and J. W. Stansbury.

Relationship Between Subsurface Damage and Wear of Dental Restorative Composites. J. E. McKinney and W. Wu.

Effect of Hygroscopic Diluents on the Properties of Cured Composites. K. Dermann, N. W. Rupp[3] and G. M. Brauer.

A Practical Test to Evaluate the Castability of Dental Alloys. R. P. Whitlock , R. W. Hinman[1], G. T. Eden[1], J. A. Tesk, G. Dickson, and E. E. Parry[1].

Temperature Dependence of Shear Viscosity for Several Dental Porcelains, J. A. Tesk, R. W. Hinman[1], R. P. Whitlock[1], A. D. Holmes, E. E. Parry[1].

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

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Development of more efficient, less toxic polymerization accelerators indicates much promise for the generically biocompatible 4,4,N-diethylaminophenylacetic acid which is reactive at four fold reduced concentration relative to currently used amines. Raman, IR and ^{13}C NMR spectroscopy and DSC are being compared for investigation of dental resin polymerization. Solvent carrier and amine catalysts have been shown to influence stability of silane-silica bonding in composites. A state-of-the-art report on radiopaque plastics in dentistry was prepared. A silver staining technique developed to assist investigation of mechanisms of degradation and wear in composite restorations yields useful information on subsurface microdefects in <u>in vivo</u> and <u>in vitro</u> worn specimens. <u>In vitro</u> wear with a pin-on-disc machine indicates increased wear of a composite is generated by going from a very hard (apatite) pin to a softer (stainless steel) pin. A wear test placing greater emphasis on shear forces generated via food particle interplay with teeth has been developed. With thermal expansion measurements, significant differences in the excess volume retained on cooling porcelains fired as per manufacturers' recommendations were noted. Gap and shape changes in a porcelain veneered to alloy split ring offer promise for determining compatibility of porcelains for alloys.

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

Accelerator; alloy; base metal; casting; composite; cyanoacrylate; dental alloy; initiator; resin; wear.

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