NBSIR 82-2623 (NIH)

# Properties and Interactions of Oral Structures and Restorative Materials

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Materials Science
Polymer Science and Standards Division
Dental and Medical Materials
Washington, DC 20234

Annual Report for Period
October 1, 1981 thru September 30, 1982

Issued December 1982

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# PROPERTIES AND INTERACTIONS OF ORAL STRUCTURES AND RESTORATIVE MATERIALS

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W. Wu, and J. E. McKinney

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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# ABSTRACT

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

(1) New polymeric formulations designed to reduce curing shrinkage, residual unsaturation and hydrophilicity in dental composite restorations have been developed. A high molecular weight, moderately viscous polythiol, pentaerythritol tetra(3-mercaptopropionate), not only contributes toward this goal but improves both color and color stability.

(2) The recently reported dental cements based on esters of vanillic acid have now been shown to have excellent long term solubility characteristics. Modification of formulations yields uniquely high strength properties. Their potential for development of higher strength intermediate restorative resins has been demonstrated.

(3) Deterioration of composite restorative materials exposed to solvents that simulate food debris was shown to be maximal in 75% ethanol-water solutions as judged by silver stain examination of the microdefect regions, changes induced in surface hardness and wear loss as measured by a pin on disc apparatus.

(4) Supporting the hypothesis that environmental factors, i.e. food-derived oral components, are the key antagonists to improved durability of composite restorations is the knowledge that the resin matrix as cured at 37°C has a low degree of polymerization (DP) and hence is more susceptible to softening by penetrating molecules. Infrared spectroscopy measurements have now shown that the DP in a given composite is more sensitive to monomer composition than to initiator type or concentration. The rate of solvent induced softening of composites has been demonstrated to depend on the temperature at which the composite is cured.

(5) To overcome some of the dissatisfaction with existing porcelain-metal bond strength (PMBS) tests, a bending beam composite specimen was designed and initial four point bending results obtained in collaboration with several dental manufacturers indicate the potential for a simple, reproducible, and informative test method.

(6) Using a recently developed alloy castability test method, it has been shown that castability values are strongly dependent on mold and alloy temperatures and that observations of the castability value standard deviation can be used to optimize casting conditions.

# SUMMARY

New polymeric formulations designed to reduce curing shrinkage, residual unsaturation and hydrophilicity in dental composite restorations have been developed and evaluated. To reduce polymerization shrinkage emphasis has been placed on high molecular weight bulky monomers such as blends of BIS-GMA and diurea dimethacrylate types. While typically moderate to fast-acting accelerators such as bis(N,N-2-hydroxypropyl)p-toluidine or p-tert-butyl-N,N-dimethylaniline could not be used with such formulations, substitution of slower acting accelerators such as ethyl-4-dimethylaminobenzoate or ascorbyl palmitate yielded formulations that set in clinically acceptable times. Powder/liquid, paste/paste or single paste/visible light cured formulations produced composites with excellent physical and esthetic properties.

To achieve a lower residual unsaturation in composite resin matrices without increasing the polymerization shrinkage as occurs when methyl methacrylate serves as monomer diluent, combinations of bicyclic mono methacrylates such as isobornyl methacrylate with a highly fluorinated, multifunctional prepolymeric methacrylate (PFMA) were examined. The latter, having a molecular weight of approximately 10,300 and a high fluorine content, helps to reduce polymerization shrinkage and impart hydrophobic character to the cured composite. Rather low strength properties in these composites were improved only slightly by using a glass filler that had been not only silanized but also treated with a fluorinated silane agent. Substitution of crosslinking dimethacrylates for the isobornyl methacrylate and retention of the highly fluorinated PFMA along with a fluorinated monomer diluent yielded composites with very high fluorine content and with adequate strength properties . A

new application to dental materials of Fourier Transform Infrared Spectroscopy showed the desirably low water sorption properties of these composites.

For reduction of both residual unsaturation and polymerization shrinkage in the composite resin matrix high molecular weight polythiols such as pentaerythritol tetra(3-mercaptopropionate), PETMP, have been shown to have promise as potential non-vinyl comonomers as well as synergistic polymerization accelerators. Modest amounts of PETMP (<5% by weight) reduced unsaturation of a typical composite resin system by as much as 20 percent. Studies of PETMP with slow, moderate and fast amine accelerators demonstrated the effectiveness of the polythiol in enhancing esthetics as well as color stability. PETMP offers the means for fashioning dental resin systems with a wide range of properties, e.g. tough elastomers to rigid glasses.

Despite many inferior properties dental cements are estimated to find application in 50 percent of all dental restorative procedures. In the FY81 report (NBS IR 81-2431; PB82-195579 A08) the development of improved cements based on reaction of zinc oxide, ethoxybenzoic acid and hexyl vanillate was described. While biocompatibility data is being accumulated on such cements, new vanillate derivatives such as decamethylene divanillate and methacryloyl ethyl vanillate and esters of syringic acid have been synthesized and their incorporation into cements studied. The latter compounds were included since syringic acid had earlier been shown to have caries inhibiting effects in rats. Strength, adhesion and solubility properties of some of these cements are equally or more promising than those obtained with the hexyl vanillate. The hexyl vanillate type cements have the unique property of not inhibiting polymerization of dental resins (in contrast to the eugenol cements they are designed to replace). Therefore investigations have been conducted to modify these cements by inclusion of a polymerizable monomer system as a means for developing improved intermediate restorative materials. By this technique cements with strengths three to six times that of comparable eugenol cement formulations were achieved. Particularly promising as an intermediate restorative liquid component is a formulation consisting of hexyl vanillate, ethoxybenzoic acid, dicyclopentenyloxyethyl methacrylate and methyl methacrylate.

Our recent demonstration (1) that a subsurface damaged region exists in clinically worn composite restorations, (2) that the microvoids generated in this region are isotropic and not of a stress-induced preferred orientation, (3) that microvoids exist throughout the resin matrix as well as in the filler/resin interface region, and (4) that immersion in food simulating chemical solvents covering a rather wide range of solubility parameters will induce a form of damage similar to that observed in the clinical specimens has shifted the emphasis in "wear" research to the resin component of composites. A classical pin on disc wear test (described in previous reports) and an erosion technique provide accelerated testing of specimens degraded in a manner believed to simulate <u>in vivo</u> degradation processes. Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Small Angle X-ray Scattering (SAXS), and the silver staining procedure have all been brought to bear in an analysis of the mechanisms governing the durability of composite restorative materials.

Supporting the hypothesis that environmental factors, i.e. food-derived oral components, are the key antagonists to improved durability of composite restorations is the knowledge that the resin matrix as cured at 37°C has a low degree of polymerization and hence is more susceptible to softening by penetrating molecules. FTIR measurements have now shown that the degree of polymerization, DP, in a given composite is more sensitive to monomer composition than to initiator type or concentration. Such measurements have also been used to project the maximum DP that can be expected to be attained in a year at 37°C as well as the extent of increase in DP that is achievable at higher initial curing temperatures. Knoop Hardness measurement of composites immersed in food simulating solvents showed that the rate of solvent-induced softening of the composites depends on the temperature at which the composites are cured. *In vitro* wear results on solvent immersed composites corroborate the hardness measurement data and reinforce the need to improve resin resistance to such attack.

A critical factor in the clinical performance of porcelain fused to metal restorations is assumed to be the strength of the bonding. Existing tests for bond strength have deficiencies that have inhibited their application universally. In an attempt to overcome some of the principal difficulties with these tests, a bending beam composite specimen was designed for evaluation. The specimen is prepared to provide all smooth surfaces at porcelain-metal junctions and when subjected to the proper bending moment, creates tension at the bond and within the porcelain. Theoretical beam model stress calculations were checked by the finite element method and showed smooth transition in surface stress across the interface. Initial experimental data obtained in collaboration with three dental manufacturers indicate the potential for a simple, reproducible and informative test method.

A castability test for dental alloys that evolves a castability value, $C_v$, by determination of the percentage of cast alloy segments that comprise a rectangular grid, is shown to be useful in optimizing casting conditions. The castability value defines what can be expected for an alloy used under controlled conditions in a dental laboratory. In a study of the effects of mold and alloy temperatures, the dependence of $C_v$ on temperature was clearly indicated. For each alloy examined an optimal mold and casting temperature could be discerned beyond which castability values changed very little. The degree of "superheat" required to produce the optimal casting temperature is unique to each alloy. As the limiting value for castability is approached ($C_v$ = 100 percent) the standard deviation (SD) from the mean determination of $C_v$ appears to decrease. Hence, larger SD's for some alloys may be indicative of potential for further optimizing conditions for casting of that alloy.

# INTRODUCTION

The National Bureau of Standards is primarily a measurement organization. Paths of 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 has been a long standing cooperative effort both in personnel and funding, with the American Dental Association. Specific projects are carried out for the U. S. Army and a Guest Worker program with the U. S. Navy exists. 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 Command - 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 major areas of research are given below:

I. Dental Composites, Resins, Cements and Adhesion: Synthesis and Evaluation

II. Wear Resistance and Related Physical Properties of Dental Composite Restorative Materials

III. Dental Alloys and Ceramics

# I. Dental Composites, Resins, Cements and Adhesion: Synthesis and Evaluation

## A. Monomer Systems Designed to Reduce Polymerization Shrinkage, Residual Unsaturation, and Hydrophilicity

### 1. Resin Formulations of Bulky Dimethacrylates BIS-GMA + UDM

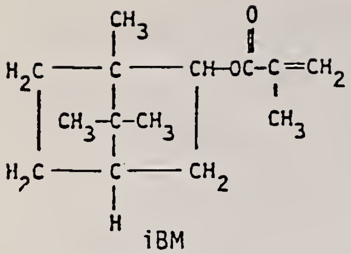
A commercial aliphatic diurethane dimethacrylate (Vivadent) prepared from trimethyl hexamethylene diisocyanate (approximately an equimolar mixture of the 2,2,4- and 2,4,4-isomers) and 2-hydroxyethyl methacrylate (HEMA) - designated by us as UDM - was shown in earlier reports to be an excellent resin for dental composites [1,2]. Composite formulations (e.g. powder/liquid, paste/paste) had excellent working, setting time, mechanical and esthetic characteristics. The molecular weight (470) and bulk of UDM are somewhat less than that of BIS-GMA and since UDM also contains some residual HEMA, it would be expected to have a higher polymerization shrinkage than BIS-GMA. Since the commercially available UDM does have a workable viscosity at ambient temperatures, in contrast to BIS-GMA, we decided to investigate a 1:1 blend of UDM and BIS-GMA as a means of obtaining a low-shrinking resin system of workable viscosity. Preliminary results in a powder/liquid formulation (powder/liquid ratio = 3) using low concentrations of moderate and fast-acting amine polymerization accelerators did not yield workable mixes. The moderate- and fast-acting accelerators were bis(N,N-2-hydroxypropyl)-p-toluidine (DHPPT) and p-*tert*-butyl-N,N-dimethylaniline (BDMA), respectively. With slow-acting accelerators such as ethyl-4-dimethylaminobenzoate(4-EDMAB) and ascorbyl palmitate (AP) workable composite mixes were obtainable with clinically acceptable setting times [3]. The viscous resin system, BIS-GMA/UDM, also was adaptable for use in paste/paste (peroxide-amine) and single paste/visible light formulations (powder/liquid = 3). Composites of excellent mechanical and esthetic properties resulted from the use of these techniques. For example, the paste/paste formulation using 0.3% DHPPT in the amine paste and 1% benzoyl peroxide silanized glass in the peroxide paste gave, with equal parts of each paste, is a composite with good handling properties, a setting time of 1.5 min., very good esthetics and color stability and a diametral tensile strength of 52.2 ± 2.0 MPa (5 specimens.) From a one minute visible light photo polymerization of a single paste formulation containing 0.2% camphoroquinone and 0.2% ethyl 4-dimethylaminobenzoate (4-EDMAB) by weight (based on the resin), composite specimens of similar mechanical properties (diametral tensile strength = 47.5 ± 1.8 MPa, 6 specimens) and excellent esthetics and color stability were obtained.

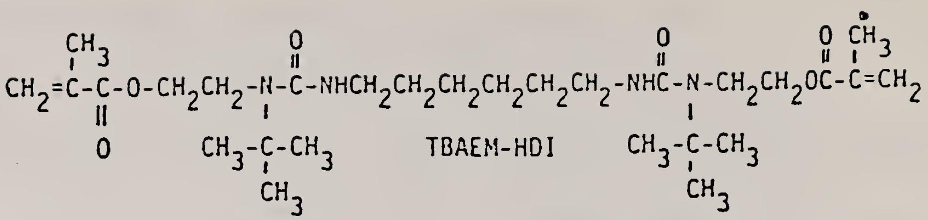
The use of high molecular weight, bulky conventional dental monomers (e.g. BIS-GMA, UDM, etc.) in resin formulations is an obvious method of reducing polymerization contraction and, thereby, minimizing residual stresses in composites and sealants. However, the highly reactive nature of such viscous dental resins precludes their use in powder/liquid or paste/paste formulations with peroxides and fast-acting polymerization accelerators without the addition of relatively large amounts of inhibitor (e.g. BHT). With moderate- and slow-acting accelerators suitable working and setting times can be obtained with these reactive, viscous resins in paste/paste and powder/liquid formulations employing peroxide initiators and low levels of inhibitor. Since photo-polymerizable composites have virtually unlimited working times, the visible light initiation systems are well suited for use with this type of dental resin systems.

### 2. Resin Formulations of PFMA and a Bulky Monomethacrylate

For conventional dental resin systems, such as those based on BIS-GMA or UDM as the major monomeric constituent, the degree of polymerization (DP) is determined to a great extent by the nature or quantity of the diluent monomer(s) used in the monomer system [4,5]. With a photopolymerized monomer system consisting of approximately 40 mol percent BIS-GMA and 60 mole percent methyl methacrylate (MMA), Ruyter and Gyorosi detected a relatively low content of unreacted vinyl groups [4]. This high degree of conversion to polymeric material was caused by the large number of readily diffusible MMA molecules present in the resin. When the resin was exposed to shortwave ultraviolet irradiation, the residual unreacted methacrylate groups was only 5%. This high degree of conversion was attributed to higher yield of radicals produced by the short wave UV exposure. This last result indicates some dependency of degree of conversion on the initiation system. With visible light we have seen similar decreases in residual vinyl unsaturation as a result of increasing time of irradiation. Unfortunately, the use of MMA as a major diluent monomer to achieve a high DP leads to a relatively high degree of polymerization shrinkage and poor marginal adaptation.

A commercially available reactive, bulky (MW=222), alicyclic monomethacrylate, isobornyl methacrylate-iBM (see structure below) was shown in previous reports to yield composites with acceptable working and setting characteristics, very good esthetics and color stability, and good mechanical properties when used as a diluent monomer for BIS-GMA or the urea dimethacrylate (shown below), TBAEM-HDI [2].

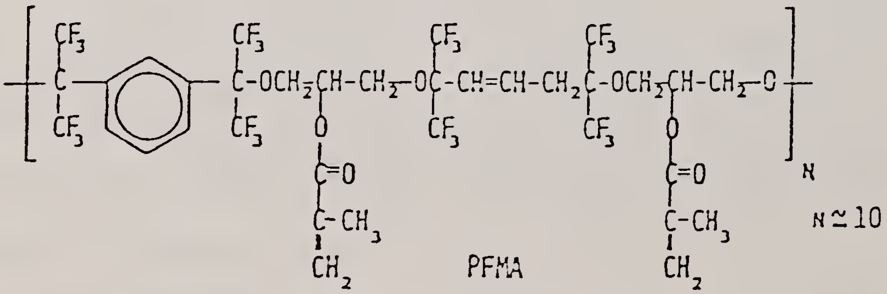

iBM


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

TBAEM-HDI

Unlike the bulky, aliphatic, long-chain monomethacrylates (e.g. lauryl and stearyl methacrylates) which have sluggish rates of polymerization compared to that of MMA at ambient temperatures, iBM seems to be even more reactive than MMA (see later section.) Another advantage of using iBM and similar alicyclic monomers over long-chain alkyl methacrylates is the stronger copolymeric matrix that results from the use of this bicyclic methacrylate. This would be expected since the homopolymer of iBM has a glass transition temperature ($T_g$) comparable to that of PMMA (110°C vs 104°C) whereas the homopolymer of stearyl methacrylate has a much lower $T_g$ (-100°C). For the same mol percent of diluent monomer and assuming a similar extent of polymerization, iBM copolymers should exhibit lower contraction on polymerization than the corresponding MMA copolymers.

The highly fluorinated prepolymer multifunctional methacrylate, PFMA (see structure below), that was synthesized in these laboratories is a novel resin that should yield dental polymeric matrices that have low surface energies and that are extremely hydrophobic and resistant to the sorption of chemical fluids derived from the mastication of food in the oral environment [6-10].



PFMA

MW OF REPEATING UNIT = 1032 AVG MW = 10,320

As is discussed at greater length in section II of this report, a likely, significant factor influencing the wear behavior of dental composites and sealants is the water-assisted diffusion of certain chemical moities derived from the presence of food in the oral environment which cause the plasticization of these polymeric materials. This chemical softening makes composites and sealants more prone to various degradative processes (e.g. chemical, mechanical, etc.) which lead ultimately to loss of anatomic form. By virtue of their high fluorine content resins based on PFMA should yield polymeric matrices having solubility parameters far removed from those of food generated oral fluids and are, therefore, less likely to be plasticized.

A problem with the viscous, polyfluorinated thermosetting resin, PFMA, has been its somewhat lower reactivity to free radical vinyl polymerization compared to conventional resins (e.g. BIS-GMA). This lower reactivity is mainly due to the lower vinyl content of PFMA but may also arise from a somewhat higher solubility of oxygen in highly fluorinated resins. By suitable adjustments in the initiator system (e.g. more active accelerators) and the type and concentration of the diluent monomer(s), PFMA-based resins with acceptable setting times (2.0-8.0 min) have been formulated. Due to its somewhat more flexible chemical nature, PFMA does not yield polymers or copolymers of as high moduli as the corresponding BIS-GMA derived polymers. However, PFMA based composites with acceptable mechanical strength have been made with the aid of the following types of diluent monomers: neopentyl glycol dimethacrylate (NPDMA), 1,6-hexamethylene dimethacrylate (HMDMA), 1,10-decamethylene dimethacrylate (DMDMA) and methyl methacrylate (MMA.)

The last formulation would be expected to yield composites with low residual vinyl unsaturation but, because of the relatively high content of MMA (33% by weight), also with a high degree of polymerization contraction. The diametral tensile strength obtained with this PFMA/MMA resin system using a powder/liquid ratio of three was 45 MPa. In view of the bulkier nature of iBM compared to MMA and the positive results obtained with this bicyclic diluent monomer and BIS-GMA or TBAEM-HDI, we investigated several formulations of PFMA with iBM. In contrast to the tensile strength results found with the PFMA/MMA formulation, none of the PFMA/iBM formulations passed the minimum ADA specification for DTS [11]. The moderate-acting accelerator, N,N-Bis(2-hydroxypropyl)-p-toluidine (DHPPT), when used without the tetrathiol, PETMP, gave at the 0.2% concentration a sluggish setting composite (>8 min). PETMP reduced the setting time significantly even at the low concentrations used in these formulations (Table 1). Higher concentrations of PETMP with PFMA/iBM resulted in the formation of emulsions indicative of the lack of compatibility of PETMP and PFMA. The relatively low mechanical strength of these composites may be enhanced by the addition of some crosslinking diluent (e.g. NPDMA) and/or the use of an initiator system that results in better cured composites. The use of F-Glass (dual silanized glass) which was prepared by a technique described in a previous report [2] improved the ease of mixing of these powder/liquid formulations and seemed to improve their mechanical strength slightly (compare formulations A and A' and C and C', Table 1.)

### 3. Resin Formulations of PFMA and Crosslinking Diluent Monomers

In Table 2 are summarized the results obtained with PFMA resin formulations employing crosslinking diluent monomers and fast-acting amine accelerators. As can be seen DTS values are enhanced significantly by the use of aliphatic hydrocarbon dimethacrylate diluents such as HMDMA, NPDMA, DMDMA and 2,2-bis[p-β-methacryloxyethoxy)phenyl]propane (BIS-EMA). The use of fast-acting amine polymerization accelerators such as p-tert-butyl-N,N-dimethylaniline (BDMA), 3,5-dimethyl-N,N-dimethylaniline (DMSX), p-N,N-diethylaminophenylacetic acid (DEAPAA) and p-N,N-dimethylaminophenethanol (DMAPE) also may contribute to the attainment of higher strength composites. Highest DTS values were obtained with Formulations 2, 2' and 3. After 7 days storage at 37°C and 100% relative humidity, composites based on formulation 3 showed a significant increase in DTS (42.4 MPa) which may indicate an increasing DP with time. The use of F-Glass did not significantly affect mechanical properties but did improve the mixing characteristics of these powder-liquid formulations. Formulation 1, which had the highly fluorinated long chain monoacrylate, pentadecafluorooctylacrylate (PDFOA), as a co-diluent, gave composites with acceptable DTS values. This PFMA based resin had the highest weight per cent of covalently bound F (approximately 36%) which is only slightly less than that of the hydrophobic resin based on octafluoropentylmethacrylate (OFPMA) and BIS-EMA (38% F) developed by Craig et al [7,8]. Formulations 3 (31% F) and 4 (33% F), had the lowest water sorption after 7 days of any composites we have studied, 0.15 mg/cm$^2$, and 0.13 mg/cm$^2$ respectively which compare favorably with that reported for the OFPMA/BIS-EMA composite (0.14 mg/cm$^2$). Use of fluorinated glass (4') did not enhance hydrophobicity. These hydrophobic composites based on fluorine-containing resins reached equilibrium with water much more rapidly (2-3 days) than conventional composites. Similar behavior was noted for the OFPMA/BIS-EMA composites

## TABLE 1

### Setting Time and Strength Properties of PFMA-IBM-Derived Composites

(Powder/liquid formulations = 3)

| Formulation of Resin | Composition | | Setting Time (min.) | Diametral Tensile Strength (MPa | Std Dev) |
|---|---|---|---|---|---|
| A | PFMA | 62.57% | 3.5 | 26.6 | 1.8 |
| | IBM | 36.17% | | (5)[3] | |
| | PETMP[1] | 1.06% | | | |
| | DHPPT[2] | 0.20% | | | |
| A' | Same as A but using dual silanized glass or F-Glass[4] | | 3.25 | 27.2 | 0.4 |
| | | | | (5) | |
| B | PFMA | 74.60% | 3.0 | 30.1 | 1.1 |
| | IBM | 23.94% | | (5) | |
| | PETMP | 1.27% | | | |
| | DHPPT | 0.19% | | | |
| C | PFMA | 62.45% | 3.0 | 23.1 | 2.5 |
| | IBM | 36.10% | | (4) | |
| | PETMP | 1.05% | | | |
| | DHPPT | 0.40% | | | |
| C' | Same as C but using F-Glass[4] | | 3.0 | 26.8 | 3.2 |
| | | | | (5) | |

[1] Pentarythritol tetramercaptopropionate

[2] N,N-Bis(2-hydroxypropyl)-p-toluidine

[3] Number of specimens

[4] Dual silanized glass (F-Glass) was prepared by a second silanization of A-174 glass using the fluoroorganic silane agent TDFOS-(1,1,2,2-tetrahydrotridecafluorooctyldimethylchlorosilane)[2]

[8]. Unlike the relatively mechanically weak OFPMA/BIS-EMA derived composites, the PFMA based composites have acceptable mechanical strength properties along with low water sorption. In addition, the polymerization shrinkage of the PFMA composites should be much lower than that of OFPMA/BIS-EMA composites.

### a. Water Sorption Studies by Fourier Transform Infrared Spectroscopy (FTIR)

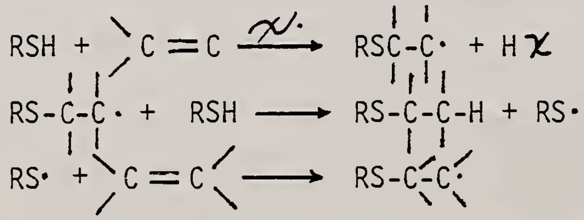
Since the water-related properties of dental composite and sealant materials may be critical factors in determining their performance in the oral environment, we have initiated a study to better understand the mechanism of the diffusion of water and related fluids into these materials. Water sorption measurements by use of near-infrared spectroscopic techniques can be a very sensitive method for assessing water uptake by composite and sealant specimens. Absorbance due to water occurs in a very transparent region of the near-infrared spectrum at 5203-5220 $\text{cm}^{-1}$ (2.0-1.9 μm). By standard methods of quantitative IR analysis, the absorbance peak due to water is directly proportional to the amount of water present in the specimen. In contrast to the determination of water sorption by the method outlined in ADA Specification No. 27 which requires immersion of a relatively large specimen in water, correction for solubility effects, long equilibration times and the measurement of small changes in large numbers, the near-IR method has the following advantages: (1) thin films which have short equilibration times can be used, (2) measurements after immersion in water versus exposure to atmospheres of 100% relative humidity (which eliminates leaching or solubulity effects) can be made, and (3) the time dependent water-sorption behavior of the specimen may be easily monitored.

The following spectra indicate the sensitivity of this method. Figure 1A shows the near-IR spectrum of a dry commercial composite (Silar) after storage in a desiccator and Figure 1B is the near IR spectrum of the same sample after exposure to an atmosphere of 100% relative humidity for 24 hours. The extreme reluctance to water uptake by composite films derived from the fluorinated resin, PFMA, (Formulation 3, Table 2) is made strikingly evident by the absence of any absorbance peak for water after the dry film is exposed to the humid atmosphere (compare Figure 2A and 2B) for 24 hours.

4. Polythiols for Reducing Vinyl Unsaturation and Polymerization Shrinkage

For reduction of residual unsaturation as well as polymerization shrinkage we have been investigating high molecular weight, moderately viscous polythiols such as pentaerythritol tetra(3-mercaptopropionate), PETMP, as a potential non-vinyl comonomer as well as synergistic polymerization accelerator.

The rationale for the use of polythiols such as PETMP to reduce the number of unpolymerized vinyl groups is based on the well known thiol/ene reaction which occurs by a free radical chain mechanism [12,13]



1) $\mathrm{RSH} + \mathrm{C{=}C} \xrightarrow{\chi\cdot} \mathrm{RSC{-}C\cdot} + \mathrm{H\chi}$

2) $\mathrm{RS{-}C{-}C\cdot} + \mathrm{RSH} \longrightarrow \mathrm{RS{-}C{-}C{-}H} + \mathrm{RS\cdot}$

3) $\mathrm{RS\cdot} + \mathrm{C{=}C} \longrightarrow \mathrm{RS{-}C{-}C\cdot}$

Where $\chi\cdot$ is an initiating radical

With olefins or polyolefins that are reluctant to propagate a

TABLE 2

Setting Time and Diametral Tensile Strengths of PFMA Composites Using Crosslinking Diluent Monomers

| Formulation | Composition of Resin (w/o) | Powder/Liquid Ratio | Setting Time (min.) | Diametral Tensile Strength MPa [Std. Dev.](No. of spec.) |
|---|---|---|---|---|
| 1 | PFMA 59.0%<br>HMDMA 15.2<br>BIS-EMA 10.0<br>PDFOA 15.2<br>DMSX 0.6 | 3 | 4.0 | 36.4 [3.0]<br>(5) |
| 2 | PFMA 69.5<br>NPDMA 28.6<br>PETMP 1.6<br>DMAPE 0.3 | 3.5 | 3.0 | 38.7 [0.9]<br>(5) |
| 2' | Same as 2 but with F-Glass | 3.5 | 3.0 | 38.8 [1.2]<br>(5) |
| 3 | PFMA 69.2<br>NPDMA 29.2<br>PETMP 1.0<br>DEAPAA 0.6 | 3.5 | 3.0 | 39.2 [2.3]<br>(5)<br>42.4 [1.0*]<br>(4) |
| 4 | PFMA 74.3<br>DMDMA 24.9<br>PETMP 0.5<br>BDMA 0.3 | 3.5 | 4.0 | 35.8 [2.9]<br>(5) |
| 4' | Same as 4 but with F-Glass | 3.5 | 4.25 | 35.3 [2.0]<br>(5) |

* After 7 day storage at 37°C and 100% Relative Humidity

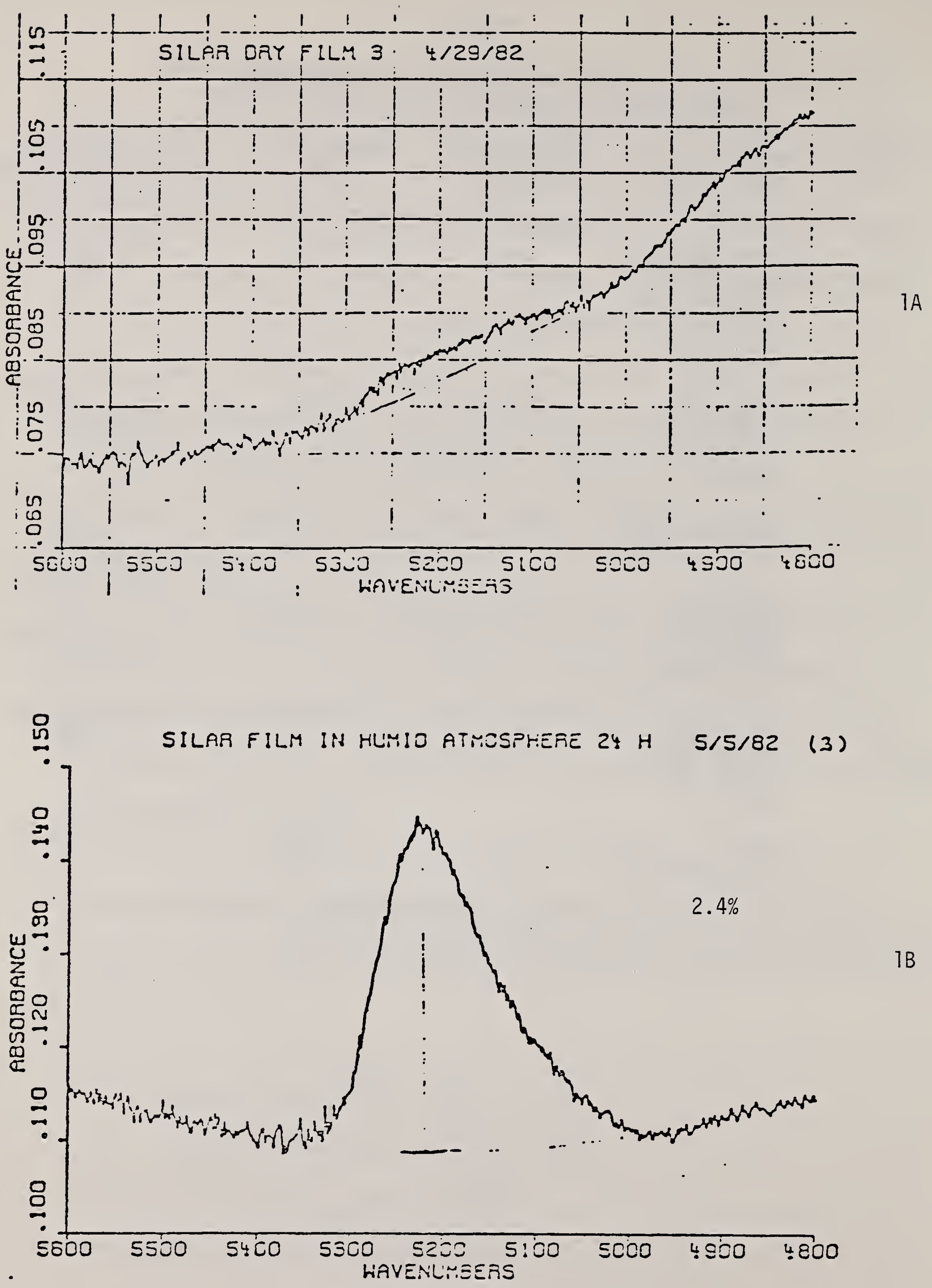
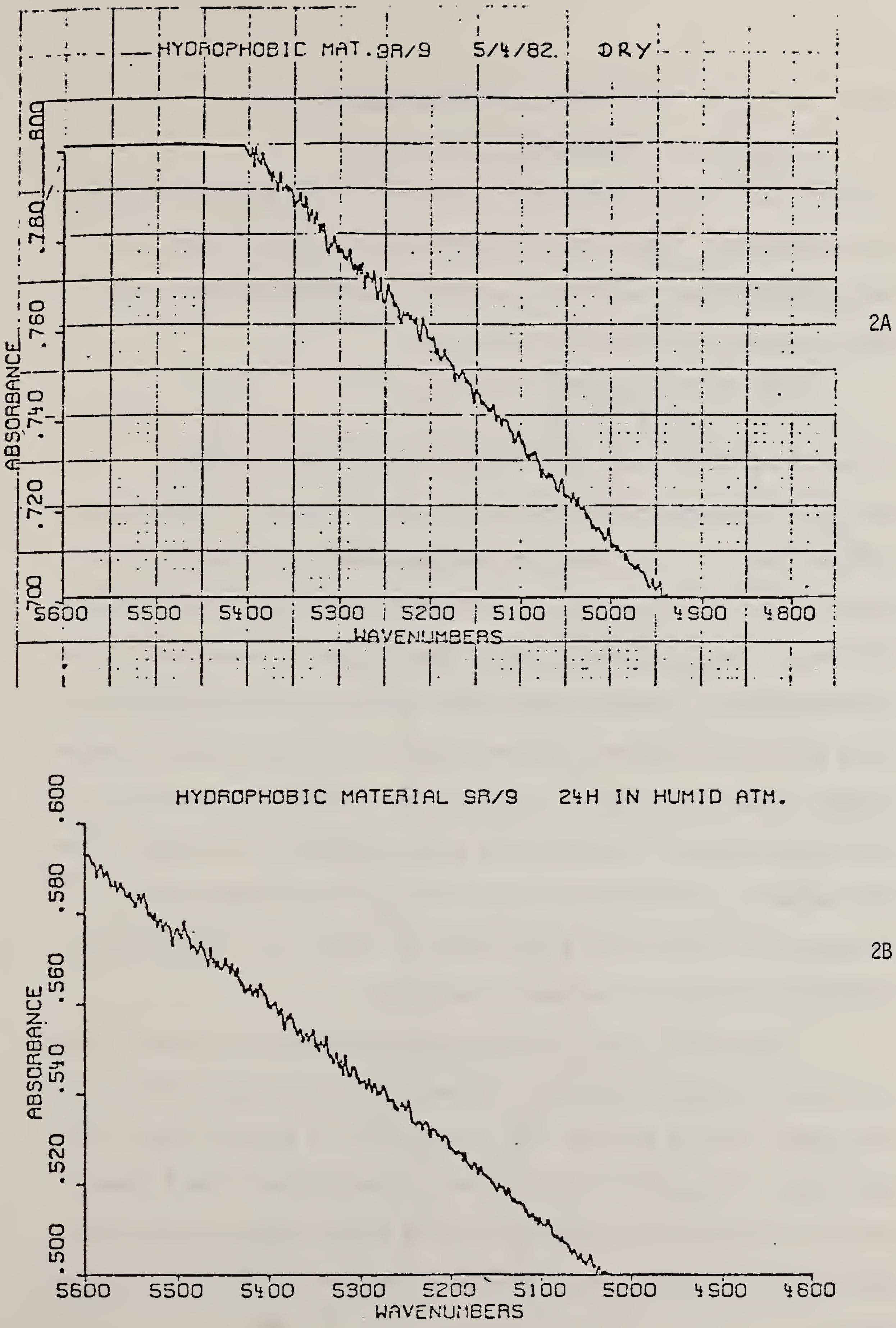

SILAR DRY FILM 3 4/29/82
ABSORBANCE
.115
.105
.095
.085
.075
.065
5600
5500
5400
5300
5200
5100
5000
4900
4800
WAVENUMBERS
1A
SILAR FILM IN HUMID ATMOSPHERE 24 H 5/5/82 (3)
ABSORBANCE
.150
.140
.130
.120
.110
.100
2.4%
5600
5500
5400
5300
5200
5100
5000
4900
4800
WAVENUMBERS
1B

Figure 1 (A & B)


HYDROPHOBIC MAT.9A/9 5/4/82. DRY
ABSORBANCE
.700
.720
.740
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5600
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5200
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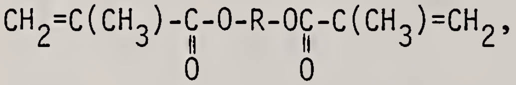
5000
4900
4800
WAVENUMBERS
2A
HYDROPHOBIC MATERIAL SA/9 24H IN HUMID ATM.
ABSORBANCE
.500
.520
.540
.560
.580
.600
5600
5500
5400
5300
5200
5100
5000
4900
4800
WAVENUMBERS
2B

Figure 2 (A & B)

polymer chain by a free radical addition mechanism, e.g.

$$CH_2=CH-CH_2-R-CH_2CH=CH_2,$$

polythiols can yield polymers by a free radical step addition polymerization mechanism. When used with multifunctional vinyl monomers that readily undergo free radical self-addition reactions of vinyl groups to create a propagating polymeric chain, e.g.



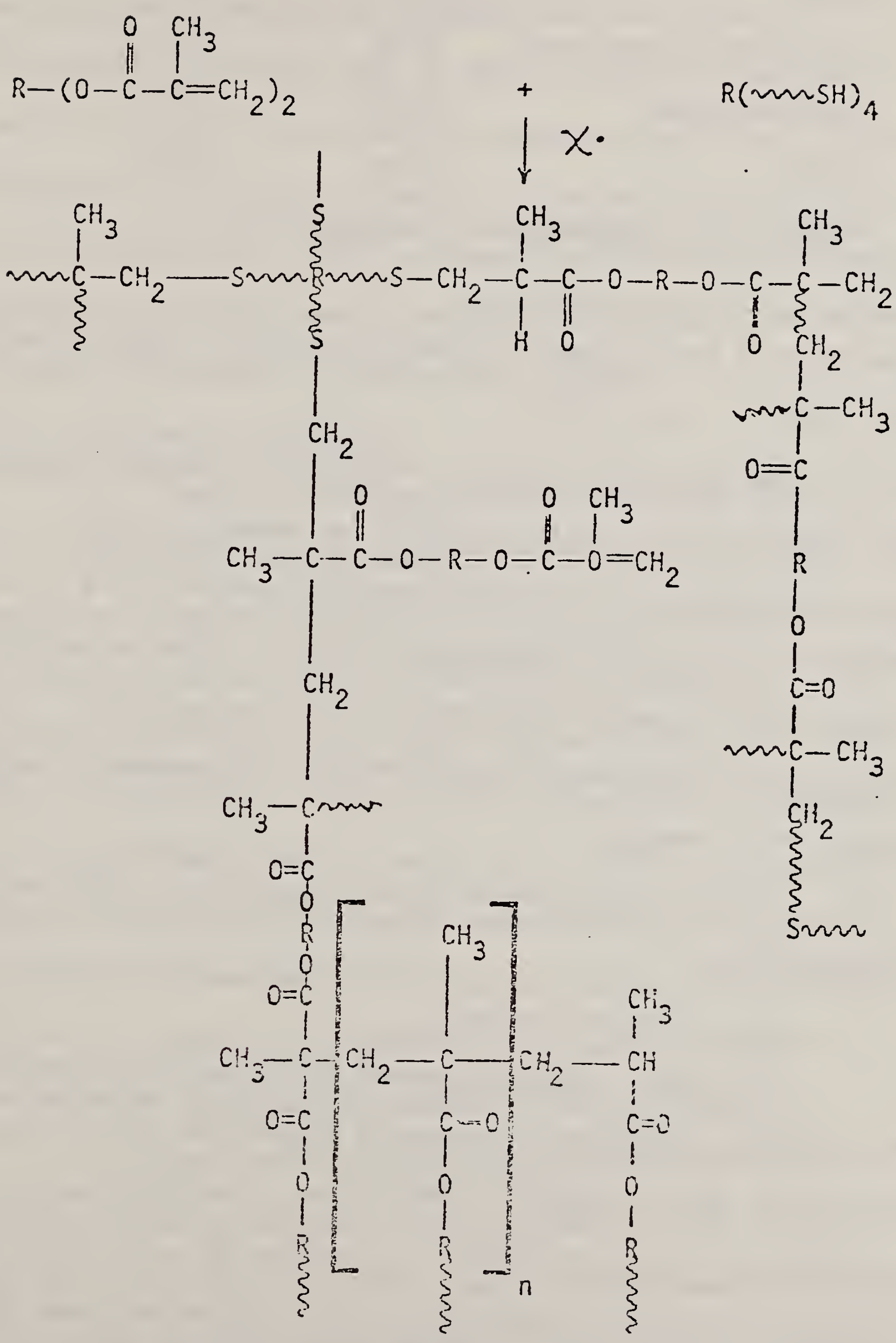
$$CH_2=C(CH_3)-\underset{\underset{O}{\|}}{C}-O-R-O\underset{\underset{O}{\|}}{C}-C(CH_3)=CH_2,$$

the use of polythiols such as PETMP leads to a hybrid polymer composed of polymethacrylate and polythioether elements in the network structure, that is a poly(methacrylate-thioether) is formed by a dual mechanism involving free radical self-addition and free radical step-addition as shown in Figure 3. Which mechanism will predominate in the polymerization will depend, among other factors, on the relative reactivity of the vinyl monomer and the polythiol and their relative concentrations. Also, the chemical, physical and mechanical properties of the resulting polymer will be determined by the molecular structures of the vinyl monomers and the polythiol and their relative concentrations. For example, using a relatively high content of PETMP (e.g. 33% by weight) with BIS-GMA yields an elastomeric copolymer.

Preliminary results using infrared spectroscopic methods indicate that there is indeed a significant reduction in vinyl unsaturation on using modest amounts of PETMP ($<5\%$ by weight) in a typical dental resin formulation. IR spectra of the two resin formulations A and B shown below were recorded, the formulations were photopolymerized using the same conditions of irradiation and the spectra obtained on the polymer films.

# POLYTHIOL/POLYENE REACTION

## CROSSLINKED POLYMER



Where X = an initiating radical

Figure 3.

| | A | B |
|---|---|---|
| BIS-GMA | 84.45 | 82.02 |
| DMDMA* | 14.90 | 14.48 |
| N,N-dimethylaminoethanol | 0.45 | 0.00 |
| Camphoroquinone | 0.20 | 0.20 |
| PETMP | 0.00 | 3.30 |

*DMDMA = 1,10-decamethylene dimethacrylate

---

Formulations A and B showed a conversion of vinyl groups to polymer respectively of 52% and 63%.

The addition of about 3% PETMP to a commercial amine-containing paste (ADAPTIC) also showed a significant decrease (8-14%) in residual vinyl unsaturation of the cured composite compared to a similar composite prepared with the usual amine paste. Adding 4% PETMP to Durafill resulted in about a 20% increase in DP after 7 days storage at 37°C. Further studies on both experimental and PETMP modified commercial dental composites are in progress.

### B. Initiator-Accelerator System Improvement: Efficiency and Biocompatibility

#### 1. Initiator Research

The benzoyl peroxide present as polymerization initiator in the paste or powder component is primarily responsible for the poor storage stability of dental composite formulations. Therefore we have endeavored to develop initiator-accelerator systems that do not utilize benzoyl peroxide as initiator. Reactivity of such systems has been determined by measurements of the setting time of composite formulations containing peroxide initiators more thermally stable than benzoyl peroxide in the tertiary amine accelerated polymerization of dental composite resins.

During this reporting period composite formulations containing t-butylperbenzoate (an initiator with longer thermal half-life than benzoyl peroxide) and N,N-diethylaminophenethanol were prepared. The effect of the addition of acids such as sorbic, benzoic or methacrylic acid on the reactivity of the initiating system was determined. It was hoped that rate of curing of the perester-initiating system would be speeded up in the presence of acids. However, with the specific compositions studied no clinically useful polymerization rates, i.e. those with cure times of less than 10 minutes were obtained.

### 2. Accelerator Research

#### a. Update on Previously Reported Efficient Amine Accelerators

During FY81 we had synthesized and evaluated a series of new tertiary aromatic amine accelerators based on derivatives of 4-N,N-dialkylaminophenylacetic acids and 4-N,N-dialkylaminophethanols [14]. These compounds proved to be very reactive in the peroxide initiated polymerization of composites. Even very low concentrations of these accelerators in the monomer lead to rapid cures. The resulting experimental composites exhibited light shades and excellent color stability. The 4-N,N-dialkylaminophenethanol has since been made available commercially. Subject to results of biocompatibility tests this amine is expected to become an ingredient of commercial dental composites.

An invited paper "Initiator-Accelerator Systems for Dental Applications" was presented at the symposium on "Initiations of Polymerization" at the 1982 Semi-Annual meeting of the American Chemical Society. The manuscript has been accepted for publication in the ACS Symposium Series.

b. PETMP as Accelerator and Reactive Diluent

PETMP*, in addition to reacting by the thiol/ene addition reaction, also can function as an accelerator for the ambient decomposition of BP. With exception of Formulation 1 (Table 5) it appears that PETMP is not an especially active promotor for the polymerization of acrylic monomers containing BP. With a fast polymerizing monomer such as BIS-GMA and in high concentrations, PETMP is an effective accelerator which also acts as a diluent comonomer. The relatively low diametral tensile strengths of the BIS-GMA (2) / PETMP (1) composites is indicative of a high content of flexible polythioether elements incorporated into the structure of the polymeric matrix. This type of composite, as expected, exhibited excellent esthetics and color stability.

<u>PETMP as a Synergistic Agent for Slow-Acting Amine Polymerization Accelerators</u>

The ethyl ester of 4-dimethylaminobenzoate (4-EDMAB) was shown in a previous study to be a slow-acting accelerator for composites prepared with the dental resin, BIS-GMA (7)/TEGDMA (3) especially when stabilized with 0.1% BHT. The effect of adding PETMP to such composites is to reduce the setting time as shown in Table 6. Another effect of PETMP is to ameliorate the effects of air inhibition on the surface cure of these composites.

<u>Effect of PETMP on Composite Formulations Using Moderate-Acting Amine Polymerization Accelerators</u>

DHPPT (Table 3) may be classified as an amine accelerator of intermediate activity, i.e. more reactive than 4-EDMAB but less reactive than BDMA or DMSX. The results of adding PETMP to powder/liquid

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* Tables 3 and 4 list the names and abbreviations pertinent to this investigation.

Table 3. Polymerization Accelerators

| Name | Abbreviation | Source |
|---|---|---|
| Ethyl 4-dimethylaminobenzoate | 4-EDMAB | Aldrich Chemical Co.<br>Milwaukee, WI |
| N,N-Bis(2-hydroxypropyl)-p-toluidine | DHPPT | Ivoclar AG<br>(Schaan, Liechtenstein) |
| N,N-Dimethyl-sym-xylidine | DMSX | Aldrich Chemical Co.<br>Milwaukee, WI |
| p-tert-Butyl-N,N-dimethylaniline | BDMA | Aldrich Chemical Co.<br>Milwaukee, WI |
| Ascorbyl Palmitate | AP | Pfizer, Inc.<br>New York, NY |
| Pentaerythritol tetra(3-mercaptopropionate | PETMP | Evans Chemetics,<br>W. R. Grace & Co.<br>Darien, CT |

Table 4. Monomers

| Name | Abbreviation | Source |
|---|---|---|
| 2,2-BIS[p-(γ-methacryloxy-β-hydroxypropoxy)phenyl]propane | BIS-GMA | Freeman Chemical Co.<br>Milwaukee, WI |
| NCO Monomer | NCO | The L. D. Caulk Co.<br>Philadelphia, PA |
| Triethyleneglycol dimethacrylate | TEGDMA | Esschem Co.<br>Essington, PA |
| 1,10-decamethylene dimethacrylate | DMDMA | " |
| 1H,1H-Pentadecafluoroctyl methacrylate | PDFOMA | Columbia Organic<br>Chemicals Co. Inc.<br>Columbia, SC |
| Isobornyl methacrylate | iBM | Polysciences, Inc.<br>Warrington, PA |
| Methyl Methacrylate | MMA | Aldrich Chemical Co.<br>Milwaukee, WI |

## Table 5

### SETTING TIMES OF EXPERIMENTAL COMPOSITES* USING PETMP AS THE ACCELERATOR AND REACTIVE DILUENT

| Formulation | Monomer System (wt. %) | Setting Time (min) | DTS in MPa [Std. Dev.] (no. spec.) |
|---|---|---|---|
| 1 | BIS-GMA (67)<br>PETMP (33) | 4.0 | 24.6 [0.9] (6) |
| 2 | NCO (93.72)<br>PETMP (6.28) | 15.0 | --- |
| 3 | BIS-GMA (64.17)<br>TEGDMA (27.50)<br>PETMP ( 8.33) | 14.0 | --- |
| 4 | BIS-GMA (48.10)<br>TEGDMA (20.60)<br>PETMP (31.30) | 14.0 | --- |
| 5 | BIS-GMA (82.18)<br>DMDMA (14.51)<br>PETMP ( 3.31) | 13.0 | --- |

* Powder/liquid formulation (P/L = 3)
Powder is silanized glass (1% BP)

## Table 6

### EFFECT OF PETMP ON THE SETTING TIME OF AN EXPERIMENTAL COMPOSITE* USING A SLOW-ACTING POLYMERIZATION ACCELERATOR (4-EDMAB)

| Formulation | Conc. of 4-EDMAB | Conc. of PETMP | Setting Time (min) |
|---|---|---|---|
| 6 | 0.50 | 0 | 8.5 |
| 7 | 0.50 | 1.17 | 8.0 |
| 8 | 0.49 | 2.16 | 4.5 |
| 9 | 0.49 | 3.54 | 6.0 |
| 10 | 0.49 | 4.86 | 5.0 |

* Powder/liquid formulations employing P/L = 3
Powder is silanized and coated with 1% BP.
Liquid consists of BIS-GMA (7)/TEGDMA (3) with 0.1% BHT and the indicated weight percent of 4-EDMAB and PETMP

composite formulations using BIS-GMA (7)/TEGDMA (3) containing diminishing amounts of DHPPT are summarized in Table 7. A synergistic accelerative effect due to the addition of PETMP is clearly evident in the reduction of setting time. Formulations D, D' and D" clearly demonstrate the benefit of PETMP as a synergistic activator for the BP/amine initiator system. The extremely small amount of DHPPT used in D" (0.0122%) along with 2.4% PETMP resulted in an acceptable composite formulation with respect to setting time and tensile strength. Without PETMP, composites prepared with this amount of DHPPT fail to meet ADA specifications (Formulation D). A doubling of the DHPPT concentration was necessary to obtain a composite formulated without PETMP that passed ADA specifications (Formulation D'). The composites prepared with PETMP all had superior esthetics compared to those formulated only with the amine accelerator.

### Effect of PETMP on Composite Formulations Using Fast-Acting Amine Accelerators

The use of BDMA in powder/liquid formulations based on BIS-GMA (7)/TEGDMA (3) containing 0.1% BHT classified this amine accelerator as highly reactive. Thus, with 0.23% BDMA and a powder/liquid ratio of 3 a very fast setting time of 1 minute was observed (diametral tensile strength = 50 MPa). In Table 8 are summarized the results of using this highly reactive accelerator with a relatively slow-polymerizing monomer system in the presence and absence of PETMP. The NCO monomer system itself (and when modified with most conventional diluent monomers) is fast-polymerizing. However, we observed that the addition of the long chain, highly fluorinated monomethacrylate, PDFOMA, moderates the rate of polymerization considerably. Thus, with this moderate-polymerizing monomer system it is necessary to use relatively high concentrations of

## Table 7

### EFFECT OF PETMP ON THE SETTING TIME AND DTS OF AN EXPERIMENTAL COMPOSITE* USING A MODERATELY ACTIVE AMINE POLYMERIZATION ACCELERATOR (DHPPT)

| ormulation | Monomer Content BIS-GMA/TEGDMA (wt. %) | Conc. of DHPPT (wt. %) | Conc. of PETMP (wt. %) | Setting Time (min) | DTS in MPa [Std. Dev.] (no. spec.) |
|---|---|---|---|---|---|
| A | 69.90/29.94 | 0.16 | 0 | 2.0 | 51.8 [2.4] (4) |
| A' | 67.60/29.00 | 0.16 | 3.24 | 40 sec | --- |
| B | 69.97/29.93 | 0.10 | 0 | 2.5 | 50.4 [1.6] (5) |
| B' | 68.43/29.30 | 0.11 | 2.16 | 1.5 | 52.2 [0.4] (5) |
| C | 69.97/29.98 | 0.05 | 0 | 3.0 | 47.7 [1.3] (4) |
| C' | 69.20/29.66 | 0.056 | 1.08 | 2.5 | 48.8 [1.7] (5) |
| C" | 68.42/29.31 | 0.055 | 2.20 | 2.0 | 47.3 [1.3] (6) |
| D | 69.99/30.00 | 0.0125 | 0 | 8.0+ | 30.0 [3.5] (5) |
| D' | 69.98/29.99 | 0.025 | 0 | 5.0 | 42.3 [1.0] (5) |
| D" | 68.32/29.27 | 0.0122 | 2.40 | 1.75 | 42.0 [3.9] (5) |

* In these powder/liquid formulations the powder/liquid ratio = 3

BDMA in order to obtain acceptable setting times and diametral tensile strengths. Because of the increased amine concentration, the esthetics of the cured composites were less than satisfactory (Formulations E and G, Table 8). The addition of PETMP to these formulations had the effect of reducing the setting times and/or the amine concentration and of significantly improving the diametral tensile strengths of the cured composites (Formulations F and H). In addition, the esthetic qualities of these composites were strikingly enhanced.

### Effect of PETMP on Composite Formulations Using Ascorbic Acid Type Accelerators

Powder/liquid formulations based on BIS-GMA (7)/TEGDMA (3) containing dissolved ascorbyl palmitate, AP, did not show any significant change in setting time as the concentration of PETMP was varied over a wide range (3.5 to 32.8%). Formulation J (Table 9) gave virtually the same setting time and diametral tensile strength as that obtained using PETMP as both reactive diluent and accelerator (Formulation I, Table 3). As the concentration of PETMP decreases, the tensile strength of the composite increases. The most salient effect of PETMP on this type of composite material is the effective stabilization against loss of accelerative activity of AP dissolved in monomer systems. After 8 months, formulations K and L, by setting time and DTS measurements, exhibited virtually no loss of accelerative potency. The esthetic qualities and color stabilities of the cured composites were excellent.

### Tertiary Accelerator Systems Based on PETMP, AP and Amine Accelerators

The effect of the addition of minute amounts of a fast-acting amine accelerator such as DMSX to a monomer system containing

Table 8

EFFECT OF PETMP ON THE SETTING TIMES AND DTS OF AN EXPERIMENTAL COMPOSITE* USING A FAST-ACTING AMINE ACCELERATOR (BDMA)

| Formulation | Monomer Content (wt. %) | Conc. of BDMA (wt. %) | Conc. of PETMT (wt. %) | Setting Time (min) | DTS in MPa [Std. Dev.] (no. spec.) |
|---|---|---|---|---|---|
| E | NCO (50.49)<br>DMDMA (39.12)<br>PDFOMA ( 9.91)<br>BHT ( 0.09) | 0.39 | 0 | 5.0 | 39.0 [3.0] (5) |
| F | NCO (49.66)<br>DMDMA (38.47)<br>PDFOMA ( 9.75)<br>BHT ( 0.09) | 0.38 | 1.65 | 2.5 | 48.0 [2.5] (4) |
| G | NCO (58.65)<br>DMDMA (31.58)<br>PDFOMA ( 9.02)<br>BHT ( 0.18) | 0.57 | 0 | 4.25 | 40.3 [3.3] (5) |
| H | NCO (57.70)<br>DMDMA (31.06)<br>PDFOMA ( 8.87)<br>BHT ( 0.18) | 0.20 | 1.99 | 4.25 | 46.1 [3.3] (5) |

* Powder/Liquid Ratio = 4

Table 9

SETTING TIMES AND DTS OF AN EXPERIMENTAL COMPOSITE* USING PETMP AND AP

| Formulation | BIS-GMA/TEGDMA (wt. %) | Conc. of PETMP (wt. %) | Conc. of AP (wt. %) | Setting Time (min) | DTS in MPa [Std. Dev.] (no. spec.) |
|---|---|---|---|---|---|
| J | 66.6/0.0 | 32.8 | 0.60 | 4.0 | 23.3 [0.9] (5) |
| K | 59.5/25.5 | 14.3 | 0.66 | 4.0 | 36.1 [1.3] (4) |
| L | 67.1/28.8 | 3.5 | 0.64 | 4.0 | 41.7 [2.2] (5) |
| M | 69.5/29.8 | 0 | 0.70 | 4.0 | 44.1 [1.6] (5) |

P/L = 3, powder is silanized glass (1% BP)

PETMP and AP is to both reduce the setting time and increase the diametral tensile strength of these composites. The results of this study utilizing the ternary accelerator system PETMP-AP-DMSX are shown in Table 10.

### PETMP as a Photoreductant for Visible Light Curable Composites

The results of this study assessing the photoreducing capabilities of PETMP are summarized in Table 11 and indicate that this polythiol is an excellent reducing agent for camphoroquinone(CQ). Preliminary experiments indicate that the photoinitiator system CQ/PETMP gives depths of cure very similar to those obtained with CQ and a tertiary aliphatic amine reducing agent such as N,N-dimethylethanolamine. The esthetics of these photocured composites is excellent. The color stability of the CQ/PETMP composites appears to be even better than that of the already excellent CQ/tertiary aliphatic amine composites.

### Storage Stability

Most of the solutions of PETMP stored well at room temperatures in glass or polyethylene vials. The BIS-GMA solution containing 33% PETMP did gel after several weeks but this could be stabilized by the addition of AP, BHT or both. The pastes containing CQ and PETMP stored well at room temperature if kept in opaque containers.

### Advantages of Using Polythiols in Dental Resins

The use of monofunctional thiols as chain transfer agents or polymerization modifiers in free radical vinyl polymerizations is well known. In essence, the chain transfer reaction involves the abstraction of the thiol hydrogen (-SH) from the mercaptan (RSH) by the radical end of a chain-growing polymer, thereby terminating the polymer chain, but creating simultaneously a new radical species, the thiyl radical (RS·), which is capable of initiating, by addition to a vinyl monomer, a new

## Table 10

### SETTING TIMES AND DTS OF EXPERIMENTAL COMPOSITES* USING PETMP, AP AND DMSX

| Formulation | BIS-GMA/TEGDMA (wt. %) | Conc. of PETMP (wt. %) | Conc. of AP (wt. %) | Conc. of DMSX (wt. %) | Setting Time (min) | DTS in MPa [Std. Dev.] (no. spec.) |
|---|---|---|---|---|---|---|
| N | 67.4/28.9 | 3.0 | 0.70 | 0.017 | 2.5 | 49.0 [1.4] (6) |
| Q | 68.7/29.4 | 1.50 | 0.35 | 0.0085 | 3.0 | 47.2 [2.6] (5) |
| R | 69.79/29.91 | 0 | 0.30 | 0 | 4.0 | 37.8 [2.3] (6) |
| S | 69.72/29.88 | 0 | 0.40 | 0 | 3.5 | 41.1 [1.6] (6) |

* P/L = 3, silanized powder (1% BP)

Table 11

## 24-HOUR DIAMETRAL TENSILE STRENGTH OF EXPERIMENTAL VISIBLE LIGHT CURED COMPOSITES* USING PETMP AS THE PHOTOREDUCTANT

| Formulation | Monomer Content (wt. %) | DTS [Std. Dev.] (No. of Spec.) |
|---|---|---|
| X | BIS-GMA (80.2)<br>DMDMA (14.2)<br>PETMP ( 5.4)<br>CQ ( 0.2) | 43.5 [1.2] (6) |
| Y | NCO (96.07)<br>PETMP ( 3.73)<br>CQ ( 0.20) | 46.5 [0.5] (5) |

*Filler is A-174 silanized 325 mesh glass; P/L = 3, time of irradiation = 60 seconds.

polymer chain. The net result is that there is a decrease in the average molecular weight of the polymer but no essential change in the rate of polymerization.

If a difunctional mercaptan is used as a chain transfer agent, the molecular weight of the polymer should be twice that obtained with a monothiol, assuming the same chain transfer constant for each thiol group. This is the case since both ends of the dithiol, after conversion to thiyl radicals ($\cdot S\text{-}R\text{-}S\cdot$), can initiate new polymer chains.

Polythiols, $R(SH)_n$ where $n > 2$ not only yield polymers with still higher molecular weights when polymerized with olefins such as methyl methacrylate, but with polyolefins (polyenes) crosslinked polymers are formed (Fig. 3). Thus PETMP and BIS-GMA undergo both chain extension and crosslinking to yield a hybrid poly(methacrylate-thioether) network structure. The inclusion of relatively large amounts of PETMP (e.g. 33%) in the dental resin yields composites having relatively low tensile strengths due to the increased flexibility introduced into the organic matrix by the high thioether content. Lowering the PETMP content of dental resins (e.g. 1- 5%) results in composites with acceptable mechanical properties. It is evident that polythiols such as PETMP can effectively replace part of the vinyl monomer content of conventional dental resin systems. By virtue of multiple free radical thiol/ene reactions, polymeric matrices having reduced residual vinyl unsaturation and, perhaps, greater oxidative stability should result.

PETMP and similar polythiols also can replace a considerable part of the amine accelerator component of dental restorative, sealant and other acrylic based materials which are polymerized by the BP-amine initiator system. Synergistic accelerator systems based on PETMP/amines lead to cured materials having enhanced esthetics and color stabilities. The mechanism of synergistic acceleration by thiols is not known but may involve regeneration of the tertiary aromatic amine by the action of PETMP on one or more primary products that result from the initial electron-transfer reaction with BP. A possible mechanism is suggested in Figure 4.

The improved esthetics and color stabilities of the cured resins are probably due in part to the prevention of the usual oxidative attack on these primary products which result in colored byproducts.

With dental resins containing the non-amine accelerator, ascorbyl palmitate, the effect of PETMP appears to be to improve the storage stability of the oxygen sensitive ascorbic acid type promotor. Conversely, AP itself acts as an effective stabilizer for monomer systems containing relatively high contents of PETMP. With extremely small amounts of tertiary aromatic amine accelerators PETMP and AP form a very effective ternary accelerator system for BP initiated polymerizations. Similar ternary accelerator systems using catalytic amounts of redox metals (e.g. copper, iron) probably can be devised to accelerate the decomposition of other peroxides, such as peresters and hydroperoxides

PETMP and other polythiols have been shown to be effective reducing agents for ultraviolet photosensitizers such as benzophenone. The mechanism involves abstraction of a hydrogen atom from the thiol group by the excited benzophenone in the triplet state to form ketyl and thiyl radicals (Figure 5). The thiyl radicals are believed to be the principal initiators of polymerization. Presumably, a similar mechanism prevails in the case of the visible light polymerization of dental resins formulated with the diketone, camphoroquinone, and PETMP.

# SYNERGISTIC ACCELERATOR - INITIATOR SYSTEMS BASED ON PETMP AND TERTIARY AROMATIC AMINES

Possible Mechanism:

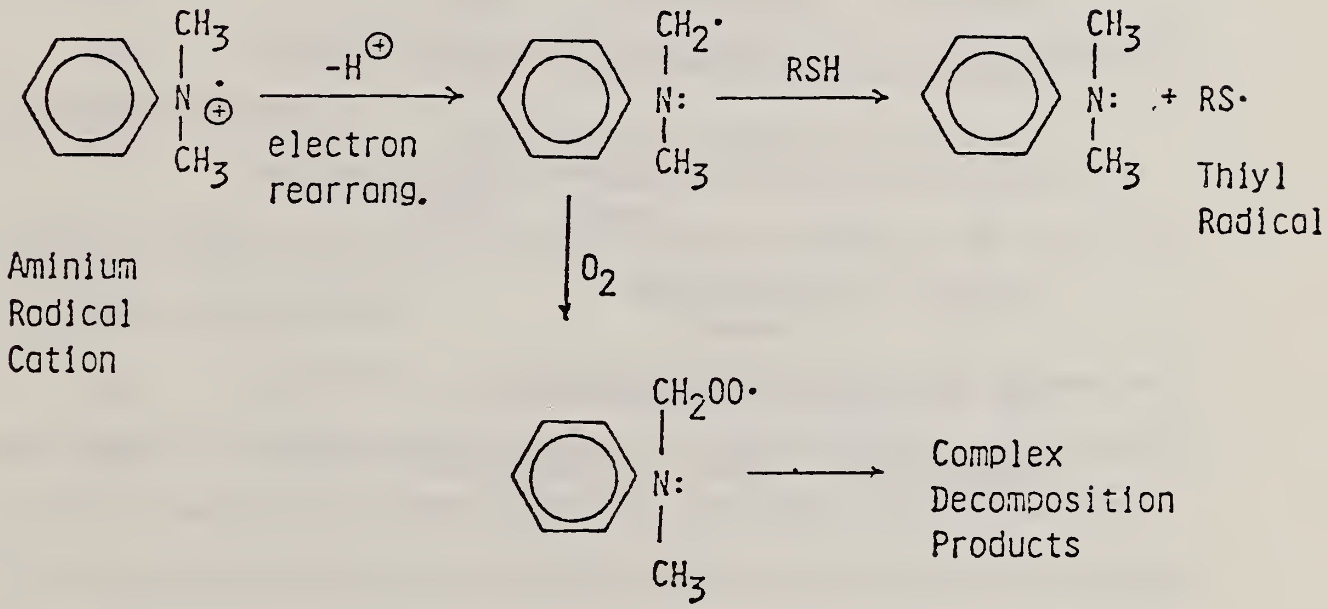


Figure 4.

Mechanism of Photoinitiation.

$$R_2C{=}O + h\nu \longrightarrow R_2C{=}O\ {}^1(n,\pi^*) \qquad \text{singlet} \tag{1}$$

$$R_2C{=}O\ {}^1(n,\pi^*) \rightsquigarrow R_2C{=}O\ {}^3(n,\pi^*) \qquad \text{triplet} \tag{2}$$

$$R_2C{=}O\ {}^3(n,\pi^*) + R'SH \longrightarrow \underset{\substack{\text{ketyl}\\ \text{radical}}}{R_2\dot{C}OH} + \underset{\substack{\text{thiyl}\\ \text{radical}}}{R'S\cdot} \tag{3}$$

$$2R_2\dot{C}OH \longrightarrow \underset{\text{pinacol}}{R_2C(OH)C(OH)R_2} \tag{4}$$

$$R'S\cdot + CH_2{=}CHCH_2R'' \rightleftharpoons R'SCH_2\dot{C}HCH_2R'' \tag{5}$$

$$R'SCH_2\dot{C}HCH_2R'' + R'SH \longrightarrow R'SCH_2CH_2CH_2R'' + R'S\cdot \tag{6}$$

Figure 5.

From this study it appears that PETMP is an effective color-stable photoreductant for diketones and, therefore, can replace or supplement the tertiary aliphatic amine reducing agents currently used in visible light curable dental composites.

Since polythiols such as PETMP can be used with a variety of vinyl monomers, by proper selection of chemical structural features in both the polythiol and the polyene components and adjustment of their relative concentrations, it should be feasible to fashion dental resin systems with a wide range of properties (e.g. tough elastomers to rigid glasses.)

### Potential Benefits of Using PETMP with Denture Base and Bone Cement Materials

Preliminary experiments were conducted to assess the effect of PETMP on the ambient polymerization of MMA and iBM using the initiator system BP/DHPPT.

In several 4 ml vials containing 1 g of the monomer was dissolved the requisite amount of BP. To these solutions were added the requisite quantities of PETMP (optional) and DHPPT in the order given. The vials were sealed with teflon lined caps and stored at the indicated temperatures (22° ± 3°C or 37° ± 1°C). The progress of the polymerization was determined by visually noting the increase in viscosity by simple inversion of each vial at 3-minute intervals. The time at which no further flow of the polymerized specimen occurred was taken as the setting time. The nature of the surface cure was noted by means of a metal probe and the coloration of each specimen also was noted (See Table 12).

Table 12

POLYMERIZATION OF MONOMETHACRYLATES - EFFECT OF PETMP

| Monomer | Wt. % BP | Wt. % DHPPT | Wt.% PETMP | Setting Time (min) | Surface Cure and Color of Polymer |
|---|---|---|---|---|---|
| MMA (t=22°C) | 2.0 | 0.73 | 0 | 120 | Very tacky, yellow |
| " | 2.0 | 0.69 | 5.8 | 60 | Non-tacky, colorless |
| iBM (t=37°C) | 1.5 | 0.50 | 0 | 6 | Slightly tacky, yellow |
| " | 1.5 | 0.45 | 6.4 | <5 | Tack free, colorless |

Similar experiments were conducted with the MMA solutions and a denture base powder (PMMA with 3% BP, Esschem Co., Essington, PA) using a powder /liquid ratio of 2.

Setting Time:

The setting times for the various composite formulations used in this study were measured as outlined in ADA Specification No. 8 (Gilmore Needle Test.) The results of this preliminary study are summarized in Table 12. It is evident that the addition of relatively small amounts of PETMP (ca 6%) to a self-curing acrylic resin can have beneficial effects on the curing process and the final polymer. With the moderately reactive amine accelerator, DHPPT, and PETMP there was a marked reduction in setting time and an improvement in the nature of the surface cure of the polymer (non-tacky) resulting from the polymerization of MMA at 22°C. A noticeable exotherm occurred after about 25 minutes from the start of the polymerization. In the polymerization of iBM at 37°C, the changes in setting time and surface character of the polymer cured with PETMP, though not as dramatic as was the case for MMA, were still significant. In the polymerization of both monomers, the pronounced color formation that is a characteristic of the BP-amine initiator system in the presence of oxygen was obviated by the use of PETMP.

Both polymers prepared with PETMP appear to be uncross-linked (soluble in methylene chloride, monomer). When these polymers were dissolved in their respective monomer (e.g. MMA, iBM) containing BP and DHPPT, to form doughs, colorless polymers resulted, indicating that the PETMP moities in the original polymers also are effective in color prevention.

A preliminary study to ascertain the effects of PETMP on a typical denture base material gave results similar to those reported in Table 12 for the monomers. Thus, the addition of MMA (0.73% DHPPT) to PMMA (3% BP)gave a dough that set in 8 minutes at 37°C. With MMA (0.69% DHPPT) containing 5.8% PETMP and PMMA (3% BP), the setting time was 6 minutes. The most striking effects of PETMP again are in the excellent esthetics and enhanced color stability of the cured acrylic. Even after 7 months at ambient temperatures and lighting conditions the specimens prepared with PETMP retain their original white appearance whereas those without PETMP have darkened considerably from their original pale yellow coloration. Specimens kept at 0°C for four months have shown a similar behavior except that there has been a slight gradual yellowing in the PETMP specimens whereas the specimens without PETMP are severely discolored.

### Summary of PETMP Research

Polythiols such as pentaerythritol tetra(3-mercaptopropionate), PETMP, can be used in the formulation of novel initiator systems that result in dental polymeric materials with enhanced esthetics and color stabilities. PETMP, as a synergistic activator for benzoyl peroxide-amine initiators, drastically reduces setting times of dental resin formulations, and thereby permits the use of lower amine concentrations. In addition, PETMP enhances the storage stabilities in the dissolved state of the highly biocompatible promotors of the ascorbic acid class. Also, PETMP is an excellent color-stable photoreductant for visible light curable composites. Finally, the use of polythiols as comonomers with dental resins has the potential for reducing residual vinyl unsaturation and further enhancing the esthetics and color stabilities of polymerized acrylic materials.

## C. Composite Filler and Filler/Resin Coupling Improvement

The interfacial bonding between resin and filler is crucial to the performance of inorganic reinforced polymeric composites such as dental composite restorations [15]. This bonding is greatly improved by the addition of a coupling agent, e.g. an organic silane, that is usually applied to the surface of the filler. A systematic study of silanization procedures has been conducted in our laboratory [2]. One of the most promising silanization procedures reported in the literature [16-22] was that of Kaas and coworkers [16]. To enable us to follow the silanization process and the stability of the interfacial bonding, we employed colloidal fumed silica as a reasonable substitute for glass. Primary amines, especially n-propylamine dissolved in normal, aliphatic hydrocarbons or cyclo hexane enhanced the silanization of silica by $\gamma$-methacryloxypropyltrimethoxysilane and yielded greater and more stable silica-silane bonding.

In the present year we evaluated the effect of various procedures employed for silanizing the reinforcing agent on the aging of cured composites containing this ingredient. Aging of specimens was established from the loss of tensile strength on storage in water at 37°C. Results of these investigations are given in Table 13. Composites with filler silanized with 0.5% $\gamma$-methacryloxypropyltrimethoxysilane in cyclohexane to which 2% n-propylamine had been added had somewhat higher initial tensile strength which decreased less on storage in water at 37°C than those silanized in

## Table 13

## Effect of Silanizing Treatment of Filler on Aging of Cured Composite

| | | |
|---|---|---|
| Liquid: | BIS-GMA: 84.7% | |
| | Tetraethyleneglycol dimethacrylate | 14.9% |
| | N,N-dimethyl-p-toluidine | 0.23% |
| | Butylated hydroxytoluene | 0.2% |

Powder: Corning Glass 7724, 325 mesh, silanized[b] and coated with 1% benzoyl peroxide

| Silanizing Treatment of Glass | Tensile Strength, MPa Storage of Cured Composite in $H_2O$ | | | % Decrease in Tensile Strength | |
|---|---|---|---|---|---|
| | Initial | 54 days | 184 days | 54 days | 184 days |
| 0.5% silane in acetone | 54.5[1.7][a] | 45.7 [0.8] | 34.6 [0.1] | 16 | 36.5 |
| 0.5% silane in cyclohexane | 54.9[0.5] | 43.2 [1.2] | 37.0 [1.0] | 21.3 | 32.6 |
| 0.5% silane in cyclohexane plus 2.0% n-propylamine | 59.9[1.9] | 48.5 [1.0] | 41.9 [0.9] | 19 | 30 |

[a] Standard variation of 5 measurements

[b] γ-methacryloxypropyltrimethoxysilane

cyclohexane or acetone in the absence of amine. The dependence of the tensile strength of the cured resin on the concentration of n-propylamine in the silanizing solution is given in Table 14. A 2% solution of n-propylamine and 0.5% of the silane reagent in cyclohexane gives composites with optimum tensile strength.

## D. Dental Cement Innovations and Adhesion Research

It has been said that "dental cements are, perhaps, the weakest and least durable of all restorative materials, and have a brittle or even friable nature" [23]. Despite many inferior properties dental cements are estimated to be used in 50 percent of all dental restorations as luting agents for fixed restorations and orthodontic appliances, as a base under permanent restorations to insulate against thermal and chemical shock, as root canal fillings, and pulp capping agents and as temporary or semi-permanent restoratives. Cements in current use are far from ideal with respect to certain critical properties that determine durability in the oral cavity. They lack toughness (i.e. have a strong tendency to brittle failure), hydrolytic stability (i.e. have a strong tendency towards excessive erosion under the action of oral fluids), and (with the exception of the zinc carboxylate and ionomer glass cements) adequate adhesion to tooth structure.

### 1. Vanillate-Based Cements

#### a. Cements from Hexyl Vanillate, o-Ethoxybenzoic Acid and Zinc Oxide

While eugenol, a 2-methoxyphenol, reacts with zinc oxide (ZnO) to yield dental cements having excellent tissue tolerance, the cements

## Table 14

## Effect of Concentration of n-Propylamine in Silanization of Filler on the Tensile Strength of the Cured Composite

| | | |
|---|---|---|
| Liquid: | BIS-GMA: 84.7% | |
| | Tetraethyleneglycol dimethacrylate | 14.9% |
| | N,N-dimethyl-*p*-toluidine | 0.23% |
| | Butylated hydroxytoluene | 0.2% |

Powder: Corning glass 7724, 325 mesh, silanized in presence of n-propyl amine in cyclohexane and coated with 1% benzoyl peroxide

| Concentration of n-Propyl-Amine in Silanization - % | Tensile Strength of Cured Composites, MPa |
|---|---|
| Unsilanized | 26.3 (0.3)[a] |
| 0.5 | 54.9 (0.5) |
| 1.0 | 53.1 (0.7) |
| 2.0 | 59.9 (1.9) |
| 3.0 | 52.8 (1.5) |

[a] Standard variation of 5 measurements

would be much more useful if their solubility in oral fluids were lower, strength properties were increased and they did not inhibit the hardening of resins in dental composites with which they come in contact [24]. While much research has been conducted to replace eugenol, the use of eugenol substitutes has usually produced cements with poor physical properties. The strength and excellent biocompatibility of cements based on reaction of ZnO with o-ethoxybenzoic acid (EBA) have made them especially useful as luting agents and bases but their disintegration is too rapid to allow their employment as more permanent restorations [25-27].

During the previous year it was reported that zinc oxide mixed with vanillate esters (Table 15) such as n-hexyl vanillate (HV) dissolved in o-ethoxybenzoic acid yielded non-eugenol containing cements [2]. These cements do not inhibit free radical polymerization and adhere strongly even in water to non-precious metals, amalgams and composites. They do not disintegrate in water (6 month $H_2O$ uptake of 0.8% versus weight loss of 12.4% for a ZOE cement) and considerably exceed the requirements of the ANSI/ADA Specification No. 30 for Types II, III and IV ZOE type Restoratives.

Thus, a portion of the cement, when used as a temporary filling, can be retained as a base for acrylic resin restorations. The material with suitable modifications looks most promising as a base, temporary restorative and endodontic cement. Cementitious restoratives with drastically improved mechanical properties and which therefore could find applications as long-lasting temporary fillings were prepared by incorporating a dimethacrylate monomer, peroxide initiator, amine accelerator and glass reinforcing fillers into the cement formulations.

## TABLE 15

Synthesis and Properties of Vanillic Acid Esters

| Vanillate Ester | Method of Purification | Elemental Analysis Carbon, % Calcd | Elemental Analysis Carbon, % Found | Elemental Analysis Hydrogen, % Calcd | Elemental Analysis Hydrogen, % Found | Refractive Index $n_D^{21}$ | Boiling Point °C/Pa, Under Reduced Pressure | Melting Point °C | Yield % |
|---|---|---|---|---|---|---|---|---|---|
| n-Hexyl | distillation | not determined | | | | 1.5234 | $183\text{-}185/5\times10^2$ | <25 | 86 |
| n-Heptyl | distillation | 67.65 | 67.42 | 8.33 | 8.48 | - | $181\text{-}183/3\times10^2$ | 29.5-30 | 70 |
| n-Decyl | recrystallization from n-pentane | 70.10 | 69.99 | 9.15 | 9.17 | - | not determined | 40-40.5 | 50 |
| 2-Ethylhexyl | extraction with aq. $NaHCO_3$ and $H_2O$, distillation | 68.55 | 68.62 | 8.63 | 8.81 | 1.5174 | $192\text{-}193/3\times10^2$ | <25 | 91 |

During the current reporting period larger quantities of hexyl vanillate were prepared. Samples of the powder and liquid were then sent to a number of institutions for biological evaluation of the basic formulation. Work to determine tissue compatibility of the materials has been initiated at the Dental School, University of Indiana. Another study of the mechanism of the hardening reaction and the possible use of these materials as soft tissue packs is being conducted at Northwestern University. Properties of several other monovanillate esters are summarized in Table 15. If these toxicity and biocompatibility studies show that the materials are suitable, a number of dental schools here and abroad have expressed a willingness to conduct clinical studies. Such investigations initially should establish the potential of the materials as a base. Are the materials a palliative similar to ZOE? Do they allow the formation of reparative dentin? Can they be used clinically as a temporary restoration with final placement of a composite without total removal of the base? Can they be used successfully for cementing crowns or short-span bridges? How do the sealing characteristics of these cements compare with those of established materials and what are the possibilities as a root canal sealer? Because of the generic nature of the compositions, improvement of specific properties may be possible by minimal changes in the formulation of the cements.

During this reporting period efforts have been directed into two areas, (1) synthesis of vanillate derivatives such as purified decamethylene and other divanillates, methacryloylethyl vanillate and esters of syringic acid and their evaluation as ingredients of dental cements and (2) development of improved intermediate restoratives based on composite formulations made from hexyl vanillate (HV)-EBA-acrylic monomer and ZnO-glass powders.

### (1) Related Synthesis

#### (a) Methacryloylethyl Vanillate

Hydroxyethyl vanillate was prepared by reaction of 10.0 g (0.06 mol) vanillic acid with 6.0 g (0.06 mol) $KHCO_3$ in water. After $CO_2$ evolution the solution was filtered, the water evaporated and the potassium vanillate was dried in a vacuum oven. The salt (13.2 g, 0.06 mol) was reacted under reflux with 5.6 g (0.07 mol) of chloroethanol and 0.25 g KI in 200 ml cyclohexanone for 24 hours. The cooled solution was extracted with water and the solvent was distilled off. The residue was recrystallized from chloroform. The purified solid melted at 85-87°C (literature value 85°C).

Hydroxyethyl vanillate (8.6 g, 0.04 mol) and triethylamine (4.1 g, 0.04 mol) were added to 100 ml $CH_2Cl_2$ and 50 ml acetone. Methacryloyl chloride (4.2 g, 0.04 mol) was diluted with $CH_2Cl_2$ and added dropwise with stirring to the solution, cooled to 5°C. After addition of the reagent the solution was allowed to rise to room temperature and stirring continued for four hours. The amine hydrochloride was filtered and the solution was concentrated. The remaining material was taken up in $CH_2Cl_2$ and extracted with 15% aquous NaCl. The dried organic layer was concentrated and put through a silica gel column. Last traces of solvent were removed in a vacuum. (Yield 8.63 g, 77%). Gas chromatographic analysis indicated the product to be more than 95% pure. Since the compound polymerized on standing at room temperature, butylated hydroxytoluene (BHT) was added as an inhibitor.

Cements prepared from 3% methacryloyl ethyl vanillate (MEV) - 10.0% <u>n</u>-hexyl vanillate (HV) or 5% (MEV) - 7.5% HV, 87% EBA, 1% dihydroxyethyl-p-toluidine and 0.02% BHT inhibitor liquid as well as 1% benzoyl peroxide in the powder (P/L ratio 1.3 g/0.23 ml) cured in 6.5 min and had good strength properties (compressive strength of 67 MPa (SD 4) and 52 MPa (SD 14) and tensile strength of 6.4 MPa (SD 0.2) respectively). Some shrinkage occurred on curing of specimens which may be the result of polymerization through the methacrylate groups present in the composition.

(b) Butanediol divanillate - A mixture of redistilled butanediol (0.02 mole), vanillic acid (0.05 mole) dissolved in toluene, and tetrahydrofuran were refluxed for 42 hours in the presence of 0.25 g p-toluenesulfonic acid. No reaction took place.

In a second attempt potassium vanillate was prepared and refluxed with butanediol in cyclohexanone for 3 days. No reaction occurred.

(c) Additional Di and Trivanillate Syntheses - The diglycidyl ether of Bisphenol A (3.4 g, 0.1 mol) was reacted under nitrogen with vanillic acid (4.2 g, 0.025 mol), and 5 drops triethylamine in 10 ml tetrahydrofuran at 100°C for 18 hours. The solvent was distilled off in a vacuum around 50°C. The residue was dissolved in methylene chloride and extracted with water and 5% aq. sodium bicarbonate. On evaporation of the solvent an extremely viscous amber oil remained which proved difficult to purify.

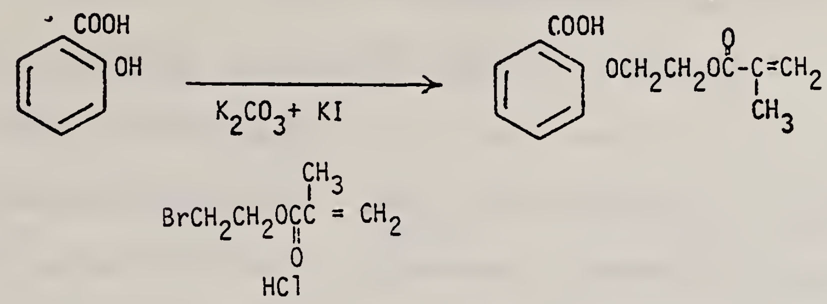
A mix of 65% ZnO - 30% $Al_2O_3$ - 6% hydrogenated rosin powder and 17% of the diglycidyl ether divanillate - 83% EBA (P/L ratio = 1.3 g/0.2 ml) was difficult to handle. It hardened in 5 min, but had a low compressive strength 19.6 MPa (SD 1.3) and a tensile strength of 7.36 MPa (SD 1.49).

Synthesis of a trivanillate from trimethylolpropane (3.35 g, 0.025 mol) and vanillic acid (16.8 g, 0.10 mol) and 0.25 g stannous oxalate was also attempted by the procedure described above. However, purification of the resulting product proved difficult. A 10% solution of the impure product in EBA when mixed with the zinc oxide powder (P/L = 1.3 g/0.2 ml) hardened in 5.5 min yielding a cement with compressive strength 33.6 MPa (SD 11.6), tensile strength 5.09 MPa (SD 0.65).

Addition of a divanillate to HV-EBA cement compositions should make it possible to obtain crosslinking. This may result in improved mechanical properties and greater insolubility of the cured cement. In previous work we have shown that the decamethylene divanillate (DDV) is more readily prepared than similar divanillates. To purify the reaction product of vanillic acid and decamethylene diol the crude dark-brown viscous divanillate, dissolved in $CH_2Cl_2$, was subjected to liquid gradient chromatography on an activated Florisil column. On successive washing with $CH_2Cl_2$, $CHCl_3$ and methanol the divanillate was eluted (MP ∿ 50°C). From its IR and NMR spectra and its analysis for carbon and hydrogen the identity of the compound was established. The high molecular weight of the divanillate made efforts to establish its exact purity by gas chromatography unsuccessful.

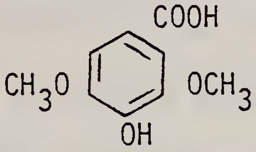
Cements prepared from 64% ZnO, 30% $Al_2O_3$ and 6% hydr. rosin powder and 11% DDV - 89% EBA at an approximate luting consistency (P/L ratio 1.3 g/0.2 ml) set in 5 min, yielding cements with compressive strength 60-70 MPa and tensile strength 7.5 MPa. The increased brittleness and somewhat higher strength properties of these cements as compared to HV-EBA cements may indicate that the DDV has crosslinking capability.

(d) Salicylic Acid Derivatives- Synthesis of a methacrylated salicylic acid capable of chelation as well as polymerization was attempted.



On refluxing the reactants a viscous dark oil formed which, after purification, could not be recrystallized from various solvents nor could it be distilled at 2 mm pressure.

### b. Cements from *n*-Hexyl Syringate



Syringic acid (3,5-dimethoxy-4-hydroxybenzoic acid) has an additional methoxy group in the 5 position compared to vanillic acid. It inhibits caries of the cotton rat by approximately 39% when 0.1% of syringic acid is incorporated into the 802 cariogenic diet [28]. On the other hand eugenol in the diet did not inhibit caries at the level tested. Although caution must be exercised when extending results on caries inhibition beyond the experimental conditions under which they were obtained, it appeared of interest to synthesize liquid or low melting esters of syringic acid. Such compounds, because of their structural similarity with vanillic acid, should form useful cements with zinc oxide. Incorporation of syringic acid into such composition could, it is hoped, make such cements cariostatic. The initial objective therefore, was to synthesize suitable derivatives of syringic acid and to evaluate derived dental cements.

To 9.91 g (0.05 mol) of syringic acid was added 10.22 g (0.10 mol) of dried hexanol and 0.1 g p-toluenesulfonic acid. To dissolve the acid 25 ml cyclohexanone was added. The mixture was refluxed for 10 hours. Since considerable unreacted syringic acid remained, more hexanol (0.1 mol) was added along with 0.1 g p-toluenesulfonic acid and cyclohexanone and refluxing was continued for an additional 24 hours. Solvent was removed by distillation. The residue was taken up in $CH_2Cl_2$ and extracted successively with aqueous $NaHCO_3$ and $H_2O$. The organic phase was vacuum distilled. A red liquid distilling at 190-220°C/3-4 mm was obtained which crystallized on cooling. Infrared spectrum of the solid indicated that this was a mixture of syringic acid with hexyl syringate. Further purification of the $CH_2Cl_2$ solution by repeated extraction with 5% $NaHCO_3$, $H_2O$, each saturated with $CaCl_2$, removal of the solvent and recrystallization from n-hexane yielded very pale yellow crystals MP=62.0-62.5°C (yield 4.2 g, 30%).

## n-Hexyl Syringate-Based Cements

n-Hexyl syringate easily dissolved in EBA. Thus, liquids containing 7-14% hexyl syringate in EBA could readily be prepared. Cements at luting consistency (1.2 g powder 0.2 mL liquid) harden rapidly (4 min) and had compressive strengths from 54 to 62 MPa (Table 16) respectively. These values are similar to those of hexyl vanillate-EBA cements. Cements with 3 to 5% n-hexyl syringate, 8 to 10% n-hexyl vanillate and 87% EBA as liquid have a lower compressive strength (38-43 MPa), but higher tensile strength (6.1 to 7.5 MPa). Their solubility is lower than that of ZOE cements. The hexyl syringate cements were quite brittle. Modification of the formulations used may improve this property.

TABLE 16

Properties of Cements Containing _n_-Hexyl Syringate

Powder: 64% ZnO - 30% $Al_2O_3$ - 6% Hydrogenated Rosin

Powder/Liquid Ratio: 1.3 b/0.2 mL

| Composition of Liquid, % | | | | Strength, MPa[a] | |
|---|---|---|---|---|---|
| _n_-Hexyl Syringate | _n_-Hexyl Vanillate | EBA (%) | Setting Time (min.) | Compressive | Tensile |
| 7 | - | 93 | 4 | 54.4 (12) | - |
| 10.5 | - | 89.5 | 4 | 62.2 (10.8) | 5.5 (1.4) |
| 14 | - | 86 | 4 | 59.2 (5.7) | - |
| 5 | 8 | 87 | 4.5 | 42.9 (6.0) | 7.5 (1.2) |
| 3 | 10 | 87 | 8 | 37.7 (12.0) | 6.1 (0.3) |

[a] Average of 5 determinations ( standard deviation.)

### c. Bonding Measurements with Vanillate Cements

The bond strength of vanillate cements to composites and non-precious metals was measured quantitatively by a modification of the procedure of Lee, et al. [29].

The thoroughly mixed cement was placed in the recessed tip of a stainless steel cylinder and was covered with a polyethylene sheet. To smoothen the surface a glass slab was pressed against the sheet. Three minutes after starting the mix the covered cylinder was placed in a 37°C - 100% relative humidity bath. Eight minutes after starting the mix a typical composite (Adaptic) was mixed and packed into a tapered mold (smaller diameter facing up) that had been coated with 3% polycrystalline wax in toluene (release agent). The cylinder containing the cement was removed from the bath 9.5 minutes after initiating the mix. The polyethylene sheet and any remaining flash were removed. After 10 minutes the cement end of the cylinder was placed against the composite. A 3 kg load was placed on the cylinder for 15 seconds. The tapered mold was stored in a 37°C - 100% relative humidity bath for 1 hour and then in water for 23 hours prior to placing the assembly into a universal testing machine. The tensile strength was determined for 5 specimens at a loading rate of 0.2 in/min.

Results of the measurements are given in Table 17. All failures were cohesive within the cement. The tensile strength of the bond was 5.5 MPa (SD 2.6) which was statistically equivalent to that obtained for the diametral tensile strength of the cement 5.0 MPa (SD 0.1). Thus, the interfacial cement-composite bond is stronger than the tensile strength of the cement. In comparison, composite bonded to a commercial ZOE cement (Fynal) had a bond strength of 0.3 MPa (SD 0.5) with all failures occurring adhesively at the composite-cement interface.

## TABLE 17

### Bond Strength of Luting Cements

Storage in water for 24 hours at 37°C

| Bond | Bond Strength, MPa[a] | Bond Failure |
|---|---|---|
| Adaptic to HV-EBA | 5.5 (2.6) | Cohesive |
| Adaptic to Fynal | 0.3 (0.5) | Adhesive |
| Pentillium bonded to HV-EBA | 4.8 (1.0) | Cohesive |
| Pentillium bonded to Fynal | 0.6 (0.8)[b] | Adhesive |

[a] Mean of all five measurements and standard deviation

[b] Stored at 37°C and 100% RH for 24 hours

For measurements of bonding to non-precious alloy the cement was coated onto flat stainless steel (Pentillium) disks. Three minutes after start of the mix the specimens were transfered to a 37°C - 100% RH bath and treated by a procedure similar to that described for the composite. The bond was ruptured cohesively. The bond strength was 4.8 MPa (SD 1.0). Specimens cemented with ZOE cement (Fynal) broke adhesively with much lower bond strengths.

### d. Heat of Setting of Vanillate-EBA-Zinc Oxide Cement

A study was conducted to determine the heat of reaction of the setting of HV-EBA-ZnO cement. The measurement was conducted in a very sensitive isothermal calorimeter having special compartments to compensate for the heat of mixing of the powder and the liquid. At 41°C a sharp peak occurred soon after mixing the components. The reaction mixture had cooled down to near its equilibrium temperature in less than 30 min. Preliminary results gave a $\Delta H=0.02$ cal/g. Thus, the reaction is rapid. Any rise in temperature on hardening is very moderate and would be of little significance clinically.

### 2. Intermediate Restorative Resins Based on Vanillate-EBA Cements

The development of high strength intermediate restorative resins takes advantage of the unique behavior of HV-EBA cements in not inhibiting polymerization. Monomeric dimethacrylates and monomethacrylates containing an amine accelerator added to the HV-EBA liquid and mixed with zinc oxide-silanized glass-benzoyl peroxide initiator powder very significantly improve the properties of the resulting cements. Mixes of these ingredients have good working properties, and a satisfactory hardening time. These HV-EBA cements, subject to tissue tolerance studies, should be useful as intermediate-term restoratives.

An immediate aim of this study was to determine the minimum concentration of monomer that must be added to the cement to obtain these high strength restoratives (Table 18). Cured cements with good working properties could be obtained that have compressive and tensile strengths respectively of 100 MPa - 200 MPa and 11 MPa - 18 MPa. The strengths of these composite cements are three to five and four to six times that of ZOE materials. Even higher strength properties can most likely be obtained by incorporating larger concentrations of dimethacrylates into the mix. It was felt that compositions with a higher percentage of monomer may not possess the desirable tissue tolerance characteristics associated with ZOE and EBA restorative materials. Thus emphasis was placed on mixes containing equal proportions of ZnO and silanized glass and HV-EBA and monomer respectively in the powder and liquid. Inspection of the results given in Table 18 also leads to the following conclusions: (1) increasing the concentration of monomer in the mix increases mechanical properties of the cement; (2) silanization

## Table 18

## Properties of n-Hexyl Vanillate-EBA Polymer Composite Cements

Ingredients:

Powder: $I_1$: 64% ZnO-30% $Al_2O_3$-6% hydrogenated rosin
$I_2$: Silanized glass coated with 1% benzoyl peroxide

Liquid: $I_3$: 12.5% n-hexyl vanillate - 87.5% EBA
$I_4$: 1,10-decamethylene dimethacrylate (DMDMA) +
1% N,N-diethylaminophenylacetic acid (DEAPAA) +
0.02% butylated hydroxytoluene (BHT)

Powder/Liquid ratio: 1.8 g/ 0.2 ml

| Composition | | | | Setting Time | Strength | |
|---|---|---|---|---|---|---|
| Powder** | | Liquid** | | (min) | Compressive MPa | Tensile MPa |
| $I_1$ | $I_2$ | $I_3$ | $I_4$ | | | |
| 2 | 1 | 1 | 1[a] | - | 137.6 (5.8)[h] | - |
| 2 | 1 | 1 | 1[b] | 9 | 127.9 (7.1) | 15.7 (1.4) |
| 2 | 1 | 2 | 1 | 7.5 | 109.9 (8.0) | 10.7 (2.6) |
| 2 | 1[c] | 1[d] | - | 9 | 49.9 (2.9) | 8.0 (1.3) |
| 1 | 1 | 2 | 1 | 7 | 118.1 (6.3) | 11.8 (1.8) |
| 1 | 1 | 1 | 1[e] | 7 | 127.0 (4.4) | 18.0 (1.9) |
| 1 | 1 | 1 | 1[f] | 10 | 131.9 (7.2) | 13.0 (0.8) |
| 1 | 1 | 1 | 2[g] | 6 | 177.9 (1.0) | 15.9 (0.8) |
| 1 | 1.5 | 1 | 1[g] | 9.5 | 150.1 (4.8) | 14.3 (3.8) |
| 1 | 1.5 | 2 | 1 | 5.0 | 132.8 (6.9) | 15.6 (0.9) |
| 1 | 2 | 1 | 2 | 4.5 | ∿199 | - |
| 1 | 2 | 2 | 1[g] | 5.0 | 136.3 (4.8) | 17.1 (3.0) |

---

* Strength of ZOE cement: compressive: 16-38 MPa; tensile: 1.4-2.5 MPa
**Parts by weight
[a] DMDMA + 0.5% N,N-dimethylpenylacetic acid
[b] DMDMA + 0.5% DEAPAA + 0.05% BHT
[c] Unsilanized glass
[d] Powder-liquid ratio 1.3 g/0.2 ml
[e] DMDMA + 0.5% DEAPAA + 0.04% BHT
[f] 5% BIS-GMA added
[g] Slurry difficulty to mix
[h] Standard deviation of 5 determinations

of the glass powder used greatly improves strength; (3) incorporation of 5% BIS-GMA with the dimethacrylate does not improve the characteristics of the cement; (4) too high a concentration of glass decreases the working properties of the mix.

The storage stability of the combined hexyl vanillate-EBA-dimethacrylate and amine accelerator liquid is not very good at elevated temperatures. Efforts were directed (1) to study the reason for premature polymerization of the combined liquids, and (2) to study the use of more storage-stable liquid systems.

Accelerated aging tests were conducted at 45°C with liquids of various compositions containing mono- and dimethacrylate monomers, different accelerators, hexyl vanillate and EBA or other acids. The formation of solid polymer on storage was observed visually. Results given in Table 19 indicate that the n-hexyl vanillate-EBA solution is very stable. Dimethacrylates can be stored with tertiary amines in the presence of inhibitors such as BHT. However, acids such as EBA when dissolved in dimethacrylates in the presence of tertiary amines lead rapidly to the partial polymerization of the monomer. The neutral diethylaminophenylacetic acid ethyl ester imparts considerably longer storage stability to the dimethacrylate-HV-EBA solution than the corresponding free acid or even N,N-dihydroxyethyl-p-toluidine.

Solutions containing methyl methacrylate monomer with HV-EBA and tertiary amine accelerators can be stored much longer at elevated temperatures than the more readily polymerizable dimethacrylates. An HV-EBA solution mixed with methyl methacrylate containing 1% dihydroxyethyl-p-toluidine and 0.02% BHT inhibitor did not polymerize within a 270 day observation period. Substitution of monomethacrylates for

## Table 19

### Storage Stability of Cement Liquids at 45°C

Liquids were prepared from equal parts, by weight.

| Composition of Liquids | | Storage Stability of combined liquid at 45° C [k] |
|---|---|---|
| Part A | Part B | |
| HV[a] | DMDMA[c] + 1% DEAPAA[e] | 60 days |
| EBA[b] | " " | 1.5 hr |
| " | " - - - - - - - | 17 days |
| 12.5% HV - 87.5% EBA | - - - - - - - - - - - | 600+ days |
| " " | DMDMA + DEAPAA + 0.02% BHT[j] | 3 hr |
| " " | " + " + 0.05% BHT | 3 hr |
| " " | " + " + 0.08% BHT | 3 hr |
| " " | " + 1% DEAPE[f] + 0.02% BHT | 1 hr |
| " " | " + 1% DMABA[g] + " | 2.5 days |
| " " | " + 1% DHEPT[h] + 0.1% BHT | 10 days |
| " " | " + 1% DEAPAA-EE[i] + " | 15 days |
| " " | MMA[d] + 1% DEAPAA-EE + 0.02% BHT | ∿180 days |
| " " | " + 1% DHEPT + " | 270+ days[l] |
| " " | cyclohexyl methacrylate | 200+ days |
| " " | QM 657[m] + 1% DHEPT + 0.02% BHT | ∿200 days |
| " " | 70% QM 657[m] + 30% MMA - 1% DHEPT + 0.02% BHT | ∿180 days |

[a] n-Hexyl vanillate

[b] o-ethoxybenzoic acid

[c] 1,10 decamethylene dimethacrylate

[d] methyl methacrylate

[e] 4-N,N-diethylaminophenylacetic acid

[f] 4-N,N-diethylaminophenethanol

[g] 4-N,N-dimethylaminobenzoic acid

[h] 4-N,N-dihydroxyethyltoluidine

[i] 4-N,N-diethylaminophenylacetic acid ethyl ester

[j] butylated hydroxytoluene

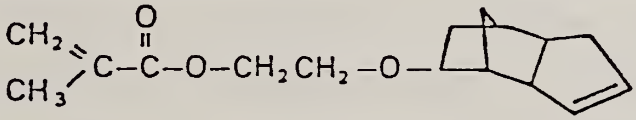
[k] time after which solid polymer had precipitated

[l] liquid had darkened

[m] dicyclopentenyloxyethyl methacrylate

dimethacrylates into the appropriate compositions yielded materials suitable as restoratives. Properties of the resulting composites are given in Table 20. Using methyl methacrylate in the liquid ingredient, cured resins with compressive strength of 130 MPa and tensile strength of 10.3 MPa were obtained. Substituting higher molecular weight, less volatile monomethacrylates yields restoratives with similar properties. However, addition of cyclohexyl methacrylate increases the curing time to 13.5 min. A composition containing isobornyl methacrylate had poor storage stability at 45°C.

By far the most satisfactory properties were obtained with solutions containing commercially available dicyclopentenyloxyethyl methacrylate (QM-657) [30]



and methyl methacrylate as monomer. The former monomer according to the manufacturer's fact sheet has low volatility. low odor, low viscosity, low curing shrinkage and is non-mutagenic. Its acute oral toxicity in rats and acute dermal toxicity in rabbits are both greater than 5 g/kg. Acute toxicity screening tests on rabbits are reported to have shown only slight irritation of the eyes and a primary skin irritation index of 2.5. Guinea pigs were not sensitized on exposure. A formulation made from a liquid containing 1 part HV-EBA and 1 part 70% dicyclopentyloxyethyl methacrylate and 30% methyl methacrylate hardens in 6.5 min. to a material having a compressive strength of 122 MPa and a tensile strength of 13.4 MPa. Furthermore, the liquid component when stored for 2 months at 45°C showed no signs of premature polymerization. A somewhat

## TABLE 20

## Properties of Intermediate Restorative Materials

Powder: 1 part: 64% ZnO - 30% $Al_2O_3$ - 6% hydrogenated rosin
1 part: silanized glass + 1% benzoyl peroxide

Liquid: 1 part: 12.5% hexyl vanillate - 87.5% EBA
1 part monomer + 1% N,N-dihydroxyethyl-p-toluidine + 0.02% BHT

Powder/Liquid ratio: 1.8g/0.2 mL

| Monomer in Liquid (%) | Setting Time (min) | Strength, MPa[a] | |
|---|---|---|---|
| | | Compressive | Tensile |
| Methyl methacrylate (MMA) | 9.5 | 129.6 (3.8) | 10.4 (0.7) |
| " " [b] | 6 | 107.9 (5.2) | 12.3 (0.3) |
| QM-657[c] | 8 | 104.3 (8.6) | 13.2 (1.7) |
| 70% QM-657 + 30% MMA | 6.5 | 122.3 (9.3) | 13.4 (0.5) |
| " + " [d] | 6 | 107.2 (10.3) | 12.1 (2.3) |
| 65% QM-657 + 25% MMA + 10% MAA | 5 | 114.3 (4.0) | 12.6 (1.6) |
| 70% " + 30% " + 1% MMA[e] | 5 | 98.2 (5.2) | 12.3 (1.9) |
| 70% " + 30% " + 0.1% MMA | 5 | 103.8 (6.2) | 10.2 (1.4) |
| 65% diclopentenyl methacrylate + 35% MMA[f] | 7 | 100.8 (10.3) | 12.5 (2.1) |
| 95% " " + 5% MMA | 6.5 | 99.1 (17.3) | - |
| Isobornyl Methacrylate | 8 | 105.3 (6.0) | 15.2 (0.2) |
| Cyclohexyl methacrylate | 13.5 | 111.3 (22.5) | 15.8 (2.0) |
| 70% Cyclohexyl methacrylate + 30% MMA | 11.5 | --- | --- |
| Commercial intermediate restorative (IRM) | 7.5 | 62 | --- |

[a] Standard deviation of 5 measurements

[b] Substituted 1% N,N-dimethylaminophenethanol for the 1% dihydroxyethyl-p-toluidine

[c] Dicyclopentenyloxyethyl methacrylate

[d] Powder composition, 1 part 64% ZnO-30% $Al_2O_3$ - 6% hydrogenated rosin;
1.5 part silanized glass + 1% benzoyl peroxide

[e] Water solubility of the cement: 0.58%

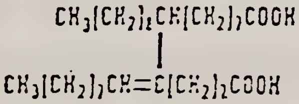
[f] Powder-liquid ratio 1.8/0.22 mL

faster cure is obtained with the addition of 10% methacrylic acid, but the strength properties of the composite are not improved. We plan to study the effect of addition of polymerizable vanillates and cross-linking divanillate as well as the effect of incorporating a silanized silica or zinc oxide powder on properties of the resulting composite.

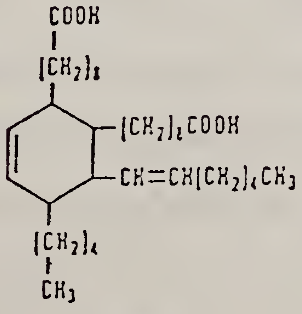
### 3. Dimer Acid Polycarboxylate Cements

The conventional polycarboxylate dental cements are based on the reaction of a liquid form of a polymeric polyacid (e.g. polyacrylic acid in an aqueous solution) with a solid basic inorganic phase (e.g. zinc oxide, etc.) to give a polycarboxylate polymer. In this case, the polycarboxylate reaction crosslinks the polymer and aids in its adhesion to tooth structure. A drawback of this dental material is its hydrophilicity.

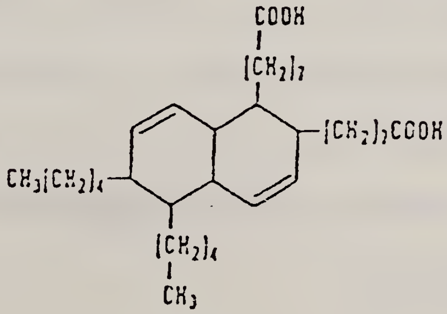
Dimer acid shown below as a complex isomeric mixture of acyclic monocyclic and bicyclic carboxylic acids, is a unique polybasic acid in its hydrophobic character and room-temperature liquidity. The latter property suggested it should be examined for dental cement applications.



Acyclic

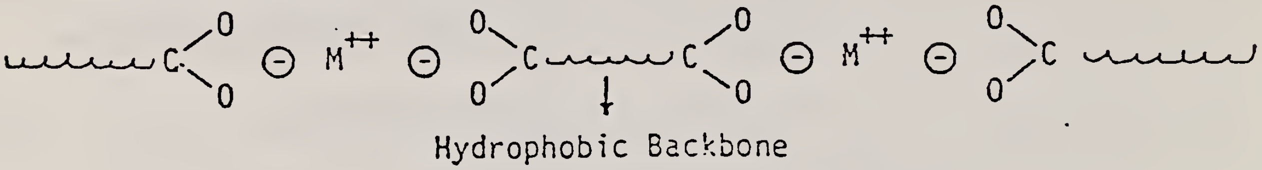


Monocyclic



Bicyclic

Polycarboxylates that are formed from dimer acids and divalent metals are linear polymers having carboxylate linkages in their backbone as depicted in a simplified fashion below;

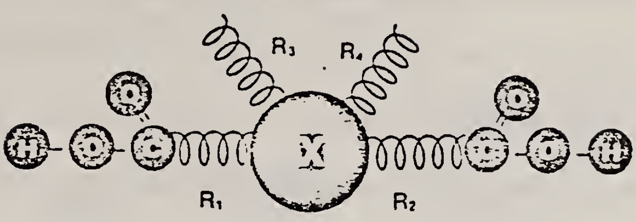


Such polymers have been prepared by fusion or metathesis [31-33].

The goal of this study was to apply the fundamental acid-base reaction mechanism of conventional nonaqueous dental cements (e.g. EBA cements) to development of tough, hydrophobic cements by the use of the bulky, flexible, hydrophobic dimer acid as the liquid component (proton donor) and various basic oxides and hydroxides as the powder component (proton acceptors).

Dimer acid (DA) is a viscous liquid produced by the dimerization of $C_{18}$ fatty acids (e.g. linoleic, oleic acids, etc.). It is a $C_{36}$ aliphatic, dibasic acid whose structure is essentially that of a long-chain dicarboxylic acid with 2 alkyl side chains ($R_3$ and $R_4$). The structure is somewhat uncertain but appears to contain at least one ethylenic bond and another linkage (X) resulting from some type of dimerization of the two olefinic fatty acid molecules that form DA. The exact nature of this linkage has not been completely defined; it may be as simple as a single carbon-to-carbon bond or as complex as a cyclic structure depending on factors such as the type of unsaturated $C_{18}$ fatty acid used and reaction conditions, such as temperature and catalyst type (see schematic below).

Schematic Structure of Dimer Molecule



| | Dimer Acid |
|---|---|
| No. of carboxyl groups | 2 |
| No. of carbon atoms | 36 |
| Approx. molecular weight | 565 |
| Approx. equivalent weight | 283 |

Table 21

Dimer Acid Cement Materials

| Components | Function | Source |
|---|---|---|
| A. Liquid - a high molecular weight liquid dibasic acid | Proton Donor (or acid) | |
| 1. Dimer Acid | | Emery Industry, Inc. |
| B. Powder - finely divided basic or amphoteric solid | Proton Acceptor (or base) | |
| 1. ZnO | | PROCOL-Sol |
| 2. MgO | | J. T. Baker Chem. Co. |
| 3. CaO | | J. T. Baker Chem. Co. |
| 4. $Ca(OH)_2$ | | J. T. Baker Chem. Co. |
| C. Fillers | Improve Dimensional Stability | |
| 1. $Ca_3(PO_4)_2$ | | Fisher Scientific Co. |
| 2. $CaCO_3$ | | Fisher Scientific Co. |
| 3. $SiO_2$ (325 mesh) | | Corning Glass Co. |

As can be seen from the above schematic structure of dimer acid, the molecule has a bulky, flexible hydrophobic structure between the terminal hydrophilic carboxyl groups. Empol 1010 Dimer Acid (Emery Industries, Inc.) is the purest grade of commercially available DA and is a polymer grade acid suitable for use as a reactant in high polymers of the polyamide, polyester, and urethane types. This acid typically contains 97% dibasic, 3% tribasic, essentially no monobasic acids, no metallic content, and an extremely low residual unsaturation. High purity and low unsaturation contribute greatly to the excellent oxidation stability exhibited by this grade of DA and its derivatives.

The high quality of this DA is exemplified by its light color and excellent color stability, two properties which are most important to manufacturers of light colored end products such as dental restorative materials and cements. Table 21 summarizes the materials used in this study and indicates their function in dental cements and their commercial sources.

The results of this study are summarized in Tables 22-24. Table 22 is a summary of the properties of DA cements formed using ZnO as the major basic component of the powder. From the standpoint of the highest strength, formulations 1, 3, and 4 are the most promising. On breaking under compression or diametral tensile stress, cylindrical specimens prepared with these formulations fractured but did not crumble into powdery debris. Some of the samples subjected to compressive stress fractured but without serious failure (that is, except for apparently minor cracks, the specimens remained intact).

## TABLE 22

## MECHANICAL PROPERTIES OF DIMER ACID CEMENTS BASED ON ZINC OXIDE AS THE MAJOR BASIC COMPONENT

| Formulation | Powder | P/L Ratio | Setting Time (min.) | 24-Hour Mechanical Strength: Compressive [Std. Dev.] (No. of Specimens) | 24-Hour Mechanical Strength: Diametral Tensile [Std. Dev.] (No. of Specimens) |
|---|---|---|---|---|---|
| 1 | ZnO | 7 | 7.0 | 49.1 [0.9] (5) | 6.2 [0.8] (5) |
| | " | 7 | 8.3 | 49.7 [3.3] (4) | 6.8 [0.2] (3) |
| 2 | " | 6 | 9.5 | | |
| 3 | ZnO(5)<br>$SiO_2^*$(2) | 7 | 9.8 | 33.5 [0.5] (5) | 5.1 [0.3] (5) |
| 4 | ZnO(6)<br>MgO(1) | 4 | 7.0 | 46.6 [1.0] (5) | 5.8 [0.8] (4) |
| 5 | ZnO(9)<br>CaO(1) | 3.5 | 7.0 | 18.4 [0.7] (5) | |
| 6 | ZnO(7)<br>CaO(1) | 3 | 6.0 | 28.7 [0.9] (2) | |
| 7 | ZnO(4)<br>CaO(1) | 2 | 7.0 | 21.4 [1.9] (4) | |
| 8 | ZnO(3)<br>CaO(1) | 2 | 5.5 | 18.6 [1.1] (3) | |

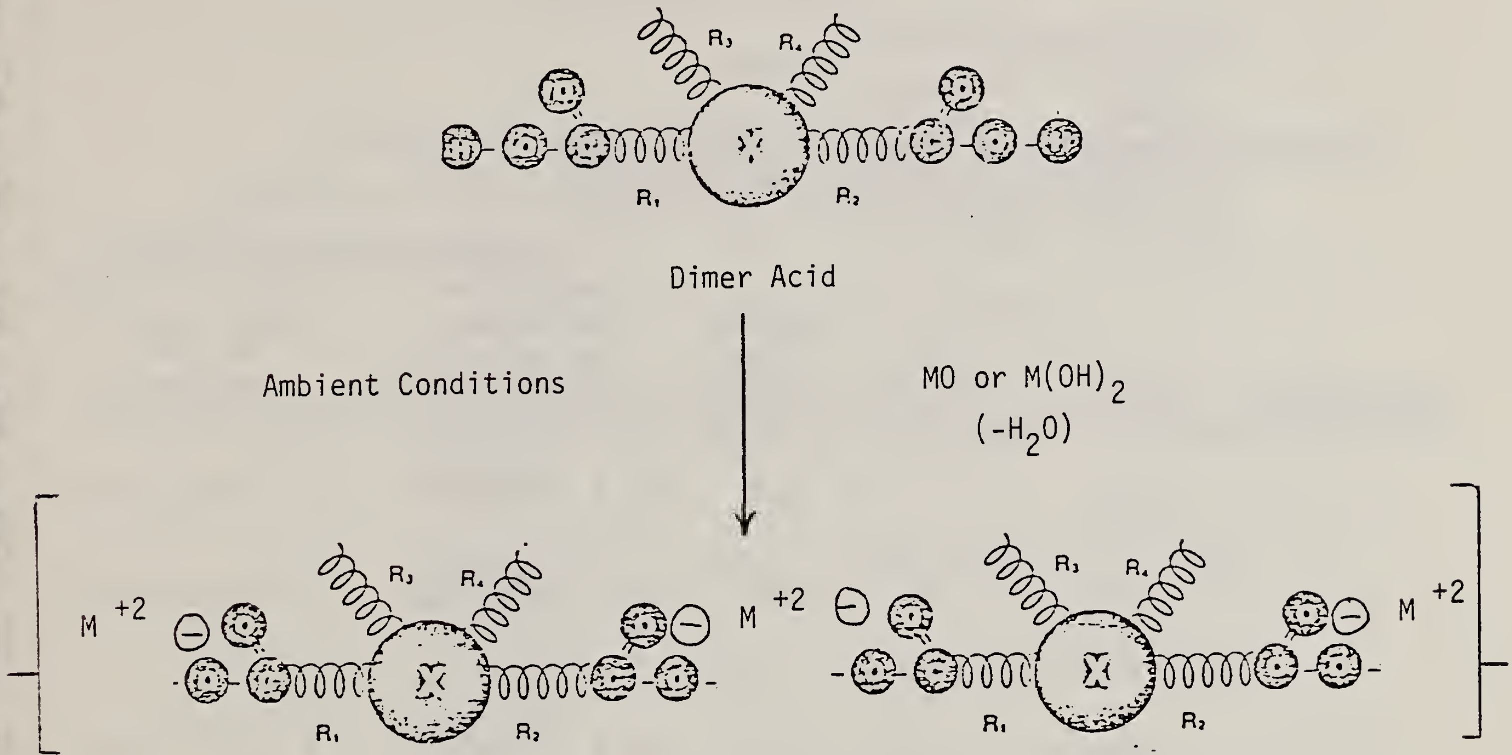
$SiO_2^*$ = glass powder (325 mesh) silanized with 2% B-carboethoxypropyltriethoxysilane.

Table 23 summarizes the properties of some cements derived from MgO and DA. Although not as strong as those prepared with ZnO, probably due to relatively low powder/liquid ratio (P/L = 1-3), these cements are strong enough to pass the ADA specification for cements.

Table 24 summarizes DA cements prepared with $Ca(OH)_2$ as the main basic ingredient. The salient feature of the $Ca(OH)_2$ cements (e.g. formulation 1) is their change in dimensions under a compressive load resulting in elastic and plastic deformation. Many of these specimens displayed only minor cracks and usually did not fracture. There was a slight recovery in dimensions on storage at 37°C for one month. The specimens formulated with fillers such as $SiO_2$ and $Ca_3(PO_4)_2$ showed only slight deformation under compressive load.

The water solubility or disintegration of the ZnO - DA cement, P/L = 7 (Formulation 1, Table 12) is only 0.1% for storage in distilled water at 37°C for 24 hours. The $Ca(OH)_c$-DA cement, P/L = 1.5 had a higher solubility in distilled water for 24 hours storage at 37°C as expected from the greater solubility of $Ca(OH)_2$ compared to ZnO. The value obtained was 1.5% which is rather good for a $Ca(OH)_2$ cement and much lower than that of a commercial cavity liner material (DYCAL). The compressive strengths of many of the DA-$Ca(OH)_2$ cements also exceed that of this widely used liner material (DYCAL).

The likely mechanism for the formation of polymerized (i.e. hardened) dimer acid cements is shown below:



Polycarboxylate cement, a linear metal carboxylate polymer M = Zn; Mg; Ca; etc......

Figure 6

The dicarboxylic acid and the divalent metal oxide or hydroxide undergo a step type acid base reaction leading to a metaloorganic polymer - specifically a linear divalent metal dicarboxylate polymer. FTIR analysis supports the above mechanism.

TABLE 23

MECHANICAL PROPERTIES OF DIMER ACID CEMENTS BASED ON MAGNESIUM OXIDE AS THE MAJOR BASIC COMPONENT

| | | | | 24-Hour Mechanical Strength | |
|---|---|---|---|---|---|
| Formulation | Powder | P/L Ratio | Setting Time (min) | Compressive [Std. Dev.] (No. of Specimens) | Diametral Tensile [Std. Dev.] (No. of Specimens) |
| 1 | MgO | 1 | 6.1 | 35.2 [1.0] (4) | 3.4 [0.6] (5) |
| 2 | MgO(1)<br>$SiO_2^*$(1) | 2 | 6.1 | 34.1 [0.4] (5) | 4.4 [0.6] (5) |
| 3[a] | MgO(1)<br>$SiO_2^{**}$(2) | 3 | 6.0 | 37.6 [1.21] (5) | 4.8 [0.7] (5) |

$SiO_2^*$ = glass powder (325 mesh) silanized with 2% 2-carboethoxypropyltriethoxysilane

$SiO_2^{**}$= glass powder (325 mesh) coated with 1% PEAA -15 from a xylene soultion. PEAA - 15 = copolymer of ethylene and 15% by weight of acrylic acid.

a - 7 day storage at 37°C instead of 24 hour at 37°C in 100% relative humidity chamber

## TABLE 24

### MECHANICAL PROPERTIES OF DIMER ACID CEMENTS BASED ON CALCIUM HYDROXIDE AS THE MAJOR BASIC COMPONENT

| | | | | 24-Hour Mechanical Strength | |
|---|---|---|---|---|---|
| Formulation | Powder | P/L Ratio | Setting Time (min.) | Compressive [Std.Dev.] (Number of Specimens) | Diametral Tensile [Std.Dev.] (Number of Specimens) |
| 1 | $Ca(OH)_2$ | 1.5 | 3.0 | 24.6 [0.5](5) | 4.2 [0.7](5) |
| 2 | Ca(OH)(2)<br>$SiO_2$*(1) | 2 | 6.0 | 23.5 [0.9](4) | |
| 3 | $Ca(OH)_2$(1)<br>$SiO_2$* (2) | 3 | 5.0 | 23.5 [0.2](2) | |
| 4 | $Ca(OH)_2$(1)<br>$SiO_2$***(1) | 2 | 4.3 | 23.0 [0.7](3) | 3.4 [0.5](5) |
| 5 ? | $Ca(OH)_2$(1)<br>$CaCo_3$ (1) | 2 | 6.5 | 22.5 [1.0](4) | 3.4 [0.3](5) |
| 6 | $Ca(OH)_2$(1)<br>$TiO_2$ (1) | 3 | 7.0 | 29.7 [1.0](4) | 5.8 [0.8](3) |
| 7 | $Ca(OH)_2$(2)<br>$Ca_3(PO_4)_2$ (1) | 2 | 6.7 | 32.0 [0.6](5) | 5.7 [0.6](5) |
| 8 | $Ca(OH)_2$(2)<br>$^aCa_3(PO_4)_2$(1) | 2 | 10.0 | 31.9 [0.8](3) | 4.8 [1.2](4) |
| 9 | $Ca(OH)_2$(2)<br>$^bCa_3(PO_4)_2$ | 2 | 7.3 | 33.4 [0.7] | 4.8 [0.5](5) |

$SiO_2$*= glass powder silanized with 2% 2-carboethoxypropyltrietloxysilane

$SiO_2$***= same glass but heated for 2 hours at 200°C

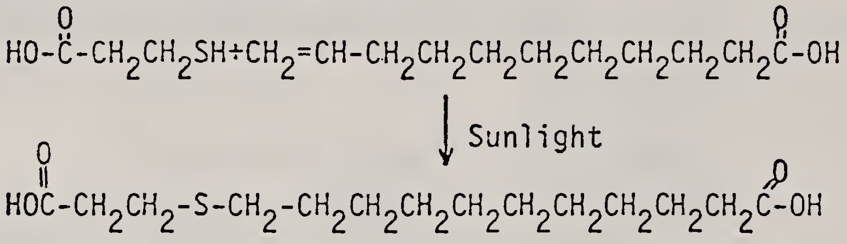
$^aCa_3(PO_4)_2$ = $Ca_3(PO_4)_2$ pretreated with DA

$^bCa_3(PO_4)_2$ = $Ca_3(PO_4)_2$ pretreated with $TiF_4$

### 4. Thiol/ene Cements

We are exploring the synthesis of high molecular weight polybasic acids (for cement applications) by means of the thiol/ene reaction. Initial experiments involved the reaction of undecylenic acid with 3-mercaptoproprionic acid and PETMP (the polythiol described in I.A.4. of this report) as shown below:

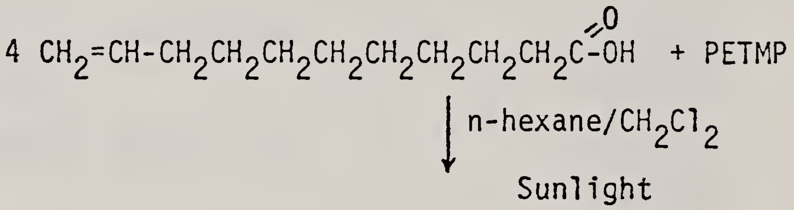
1)



$$HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2SH+CH_2=CH-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{Sunlight}} HO\overset{O}{\overset{\|}{C}}-CH_2CH_2-S-CH_2-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$$

white solid, m.p 95-7°C

2)

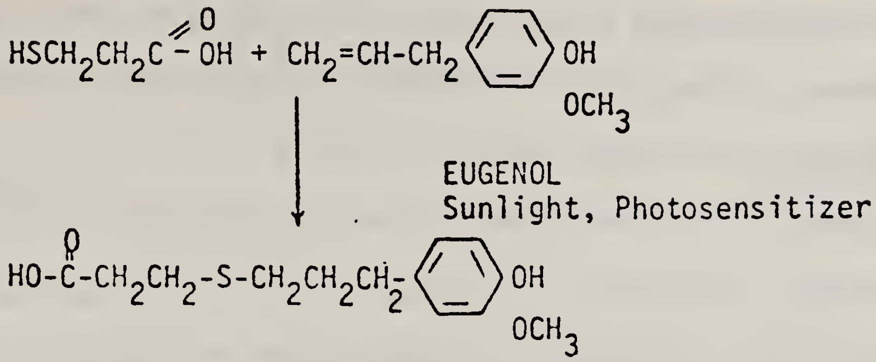


$$4\ CH_2=CH-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH + PETMP \xrightarrow[\text{Sunlight}]{\text{n-hexane}/CH_2Cl_2}$$

white solid, m.p. 63-4°C

The first reaction occurred within minutes on exposure to sunlight to give a white solid believed to be the addition product shown. The second reaction required a mixed solvent of n-hexane and methylene chloride (1:4, v/v) to obtain a homogeneous mixture. A longer reaction time at room temperature was required (about 7 hours). The work up phase yielded a white waxy solid, m.p. 63-64°C.

Another potential cement forming organic acid that we are currently synthesizing involves the reaction of 3-mercaptoprop acid with eugenol as shown below. The product is a viscous liquid.



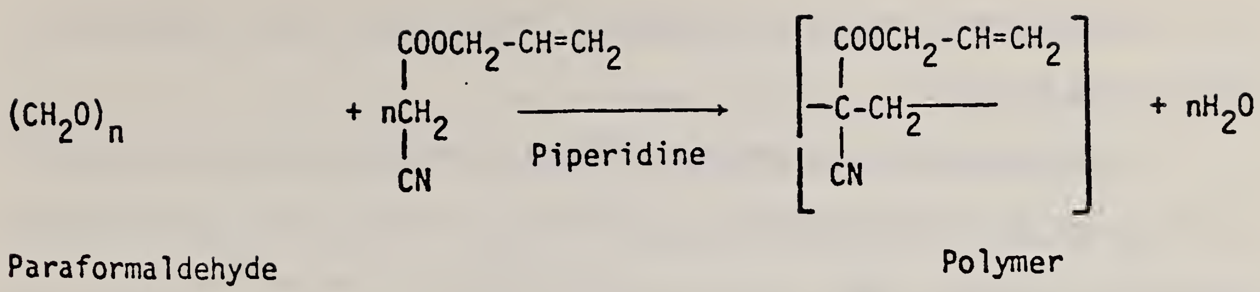
## 5. Development of Adhesive Bonding Techniques

The objective of this research has been (1) to develop a basis for clinically applicable adhesion techniques suitable for bonding polymeric materials to mineralized tissues, e.g. dentin and bone, and (2) to evaluate potential adhesive systems for their ability to serve as protective coatings or surface sealants, as liners, or as adhesives for composites and other restoratives.

Alkyl cyanoacrylates polymerize rapidly at room temperature. They form the strongest known bonds between dentin and acrylic polymers [34]. Unfortunately, weakening of these bonds takes place on exposure of the joint to water or high humidity. Monomers incorporating cyanoacrylate groups or with an allyl and a cyanoacrylate group in the molecule have been synthesized [35, 36]. These compounds polymerize anionically and crosslink when heated or when exposed to certain polymerization initiators. The resulting highly cross-linked polymer should be resistant to hydrolytic fission and possess increased hardness. Recent studies have shown that interfaces cemented with allyl cyanoacrylate have improved heat stability compared to less cross-linked cyanoacrylate joints [36]. Formulations incorporating allyl cyanoacrylates and higher alkyl 2-cyanoacrylates, difunctional aromatic diol dimethacrylate esters as well as tri(allyloxy)-s-triazine and peroxide free radical initiators have been suggested as pit and fissure sealants [37]. Adhesives containing these ingredients and suitable crosslinking agents such as p-xylene glycol bisacrylate, bisphenol A dimethacrylate have been proposed as orthodontic bracket compositions [38].

Since allyl 2-cyanoacrylate is at present not available commercially its synthesis was initiated. Allyl cyanoacetate was obtained by direct esterification of cyanoacetic acid (170.1 g, 2 mol) with allyl alcohol (162.6 g, 2.8 mol) in the presence of 3.4 g concentrated sulfuric acid and 0.17 g p-toluenesulfonic acid as catalysts and 250 ml toluene for azeotropic removal of the water formed during the reaction. After cooling the reaction mixture, a small quantity of precipitate was removed by filtration. The filtrate was extracted with 30% aqueous NaCl and 5% $Na_2CO_3$ until the aqueous extract had a pH of 7. After removing the residual solvent by mild heating, the allyl cyanoacetate was distilled at 95-96°C/5 mm. The liquid was purified by redistillation. BP=83-84°C/2.5 mm, $n_D^{22}$ = 1.4417, yield = 93.2%.

Paraformaldehyde (4.2 g) was added to 25 ml benzene and 0.05 g piperidine. This mixture was heated to reflux and then the allyl cyanoacetate (21.2 g) was added dropwise. The reaction mixture was kept basic by dropwise addition of 50% aqueous NaOH. Unreacted formaldehyde was distilled off and the solution was refluxed with excess benzene to remove the remaining formaldehyde. Finally, the solvent was distilled off.



$$(CH_2O)_n + n\underset{\displaystyle CN}{\overset{\displaystyle COOCH_2\text{-}CH{=}CH_2}{CH_2}} \xrightarrow[\text{Piperidine}]{} \left[ -\underset{\displaystyle CN}{\overset{\displaystyle COOCH_2\text{-}CH{=}CH_2}{C}}\text{-}CH_2- \right] + nH_2O$$

The polymer was dried in the presence of 1 g phosphorus pentoxide, 1 g phosphoric acid and 0.1 g hydroquinone.

A number of procedures were studied to obtain optimum conditions for the depolymerization. In the preferred method the viscous polymer containing the drying agents was distilled into a receiving flask containing 0.05 g $P_2O_5$ and hydroquinone which was cooled in a dry ice-acetone bath. The major portion of the distillate (BP 140-150°C/4mm) was collected. The crude monomer was purified by vacuum distillation. All distillation equipment was rinsed with hydrochloric acid prior to use and was then dried thoroughly. A flow of $SO_2$ was bubbled through the monomer in the flask and through the receiver. The distilled non-viscous 2-allylcyanoacrylate was stored in a bottle which had been flushed with $SO_2$. Gas chromatographic and IR analysis indicated a monomer purity of 99%. The monomer when bonded to glass had excellent adhesive properties. The availability of this monomer will allow us to formulate adhesive compositions containing this cross-linking agents as an ingredient.

## II. Wear Resistance and Related Physical Properties of Dental Composite Restorative Materials

In connection with our overall effort in developing improved composite restoratives the objective here 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 mechanical and chemical degradation processes. This information will be of use in determining the principal variables of influence for which appropriate modifications can 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, or are being, developed here which comprise a classical pin and disc apparatus and an erosion technique. (The latter was constructed during this fiscal year.) 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 Fourier Transform Infrared (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and a microdefect analysis using x-ray and optical microscopic observation of damaged regions made resolute by a silver staining technique. During this fiscal year a Mass Absorption/Desorption Analyzer was developed to measure diffusion rates of chemical solvents into polymers and dental composites.

From examination of the subsurface damage structures of *in vivo* restorations and from comparison of these structures with those which occur within *in vitro* damaged or worn composite specimens, we conclude that the chemical softening of the matrix plays an important role in the *in vivo* wear process [2, 39]. We have demonstrated experimentally that a large variety of chemicals covering a wide solubility parameter range can soften the BIS-GMA based polymer matrix [40]. Consequently similar oral substances can be expected to have a detrimental effect on the wear resistance of the composites.

The diffusion rate of chemicals in polymeric systems depends strongly on the degree of polymerization and cross-link density, both of which are known to increase with higher curing temperature in thermosetting plastics. We have therefore explored the effect of the curing temperature on the diffusion rate of chemicals within dental restorative composites.

### A. Solvent Diffusion rates in Dental Composites

The effect of four chemicals was studied on two commercial composites designated A* and B**. The specimens were cast between two glass plates and cured at either 37°C and 100°C for 24 hours. After 2, 4, and 14 days, the penetrating depth of the chemicals into the composite was measured using $Ag^+$ ions as labeling agent. The penetration depth data

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* Adaptic - Johnson & Johnson, East Windsor, NJ 08520
** Prisma - L. D. Caulk Co., Milford, DE 19963

## TABLE 25

## Effect of Curing Temperature on Diffusion Rate of Dental Composite

| Composite | Curing Temp °C | Methanol (14.5)* | | | Ethanol (12.7)* | | | Acetone (9.9)* | | | Ethyl-Acetate (9.1)* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | D | C | $r^2$ | D | C | $r^2$ | D | C | $r^2$ | D | C | $r^2$ |
| A | 37 | 45.7 | 1.0 | 0.99 | 25.2 | 0.99 | 0.99 | 62.5 | 1.0 | 0.99 | 27.2 | 0.99 | 0.99 |
| | 100 | 27.2 | 0.99 | 0.99 | 7.9 | 0.89 | 0.99 | 31.2 | 1.0 | 0.99 | 13.2 | 0.95 | 1.0 |
| B | 37 | 19.1 | 0.96 | 0.99 | 19.1 | 0.96 | 0.99 | 26.2 | 0.99 | 0.99 | 14.5 | 0.95 | 1.0 |
| | 100 | 0.33 | 0.69 | 0.43 | 0.076 | 0.60 | 0.75 | 0.97 | 0.75 | 0.75 | 2.06 | 0.82 | 1.0 |

* Solubility parameter in $(cal/cm^3)^{1/2}$

D, C: diffusion rate constants related to penetration P by $P = Dt^C$ where t is in days and P is in μm were fitted to the equation $P = Dt^c$, where P is the depth, t is the elapsed time and D and c are adjustable parameters. The resultant values of D, c and corresponding correlation coefficients $r^2$ are given in Table 25. The solubility parameter in $(cal/cm^3)^{1/2}$ of each chemical was also included in the Table.

The values of the time exponent c in Table 25 are much nearer to unity than 0.5 in almost all the cases; this result supports a Class II diffusion mechanism. The only exceptions are those data of composite B specimens cured at 100°C. The rate constant D was also dramatically reduced in those cases. The above data indicated that the diffusion rate of the chemicals in these composites and especially in composite B can be reduced significantly by increasing the curing temperature. The wear resistance of the high temperature cured composites exposed to different chemicals is being studied using the pin-disc wear equipment.

The above experimental technique is useful to identify the type of diffusion process; however, for more quantitative information regarding the saturation content of the penetrants and diffusion, an automatic Mass Absorption/Desorption Analyser was developed which operates as follows: The changes in weight of the specimens situated in a constant temperature chamber are monitored after the vapor of the penetrants is introduced. The increase in weight with time or the absorption isotherm provide the base to calculate the diffusion coefficients and the permeability parameters. The experimental equipment has been completed (Figs. 7 and 8) and the sensitivity of the weight measuring device is $10^{-5}$ gram. The output of the device is digitalized and stored on tape for further calculations.

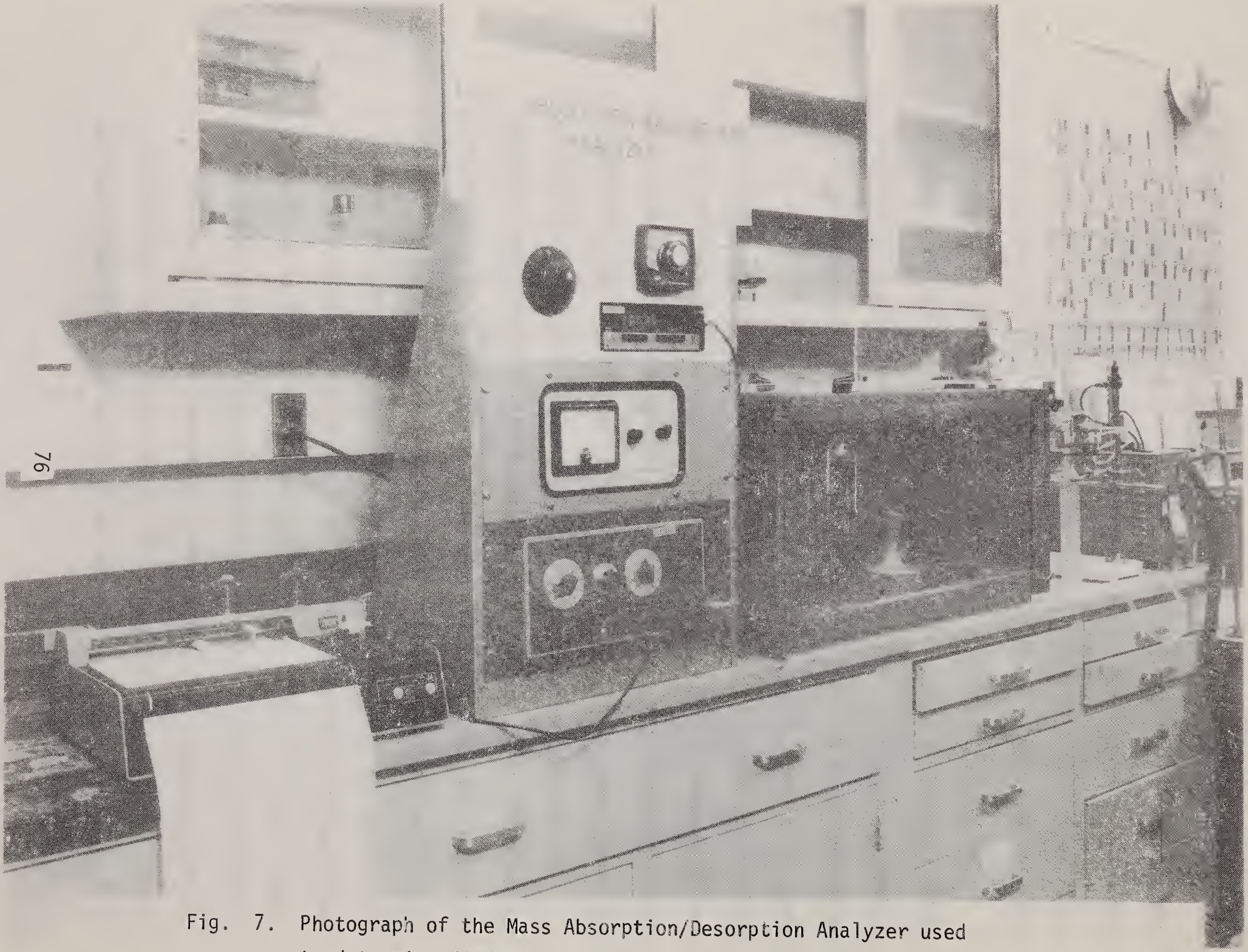


Fig. 7. Photograph of the Mass Absorption/Desorption Analyzer used to determine diffusion rates.

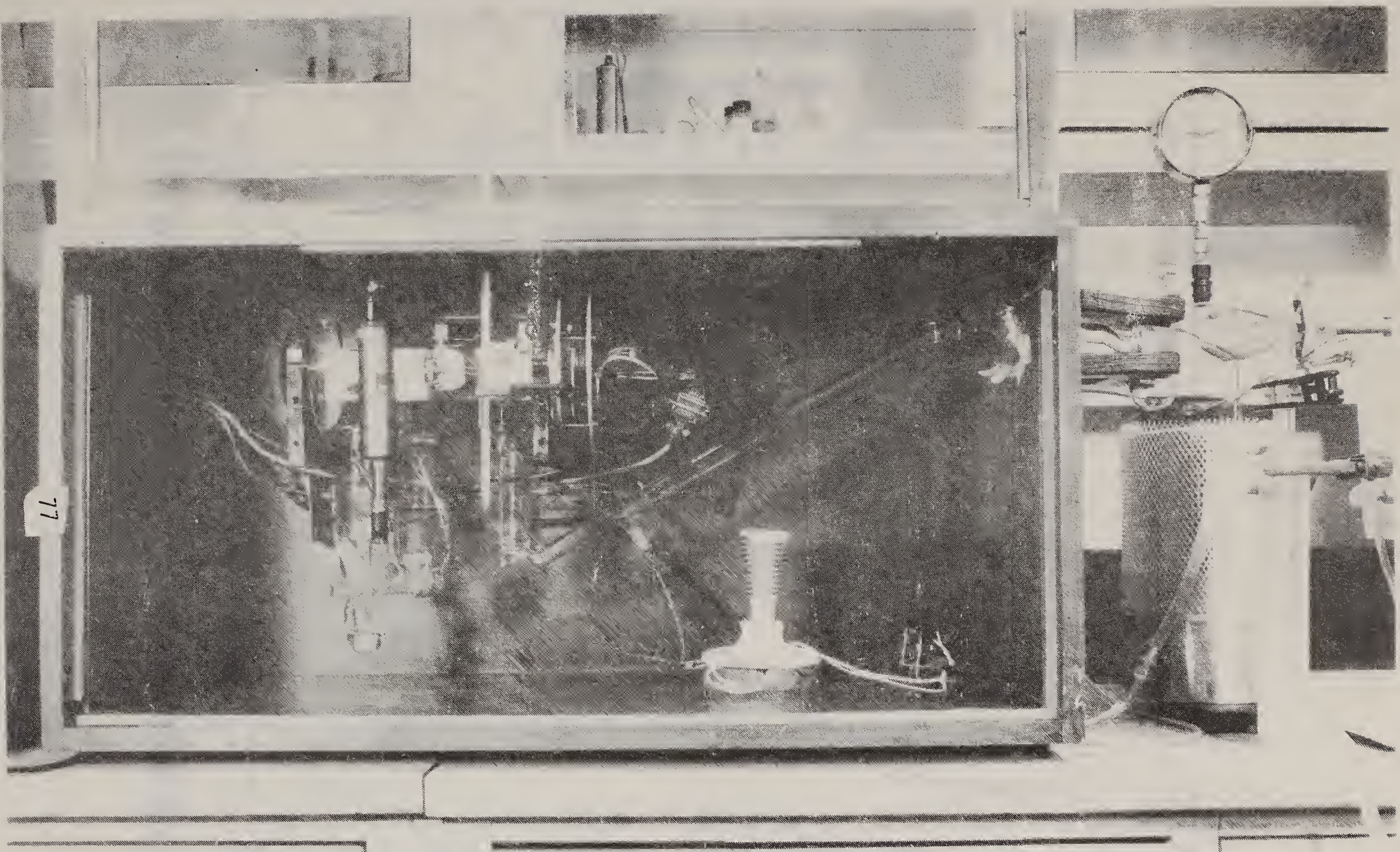


Fig. 8. Photograph of the constant temperature chamber (shown in Fig. 7) containing the automatic electrobalance.

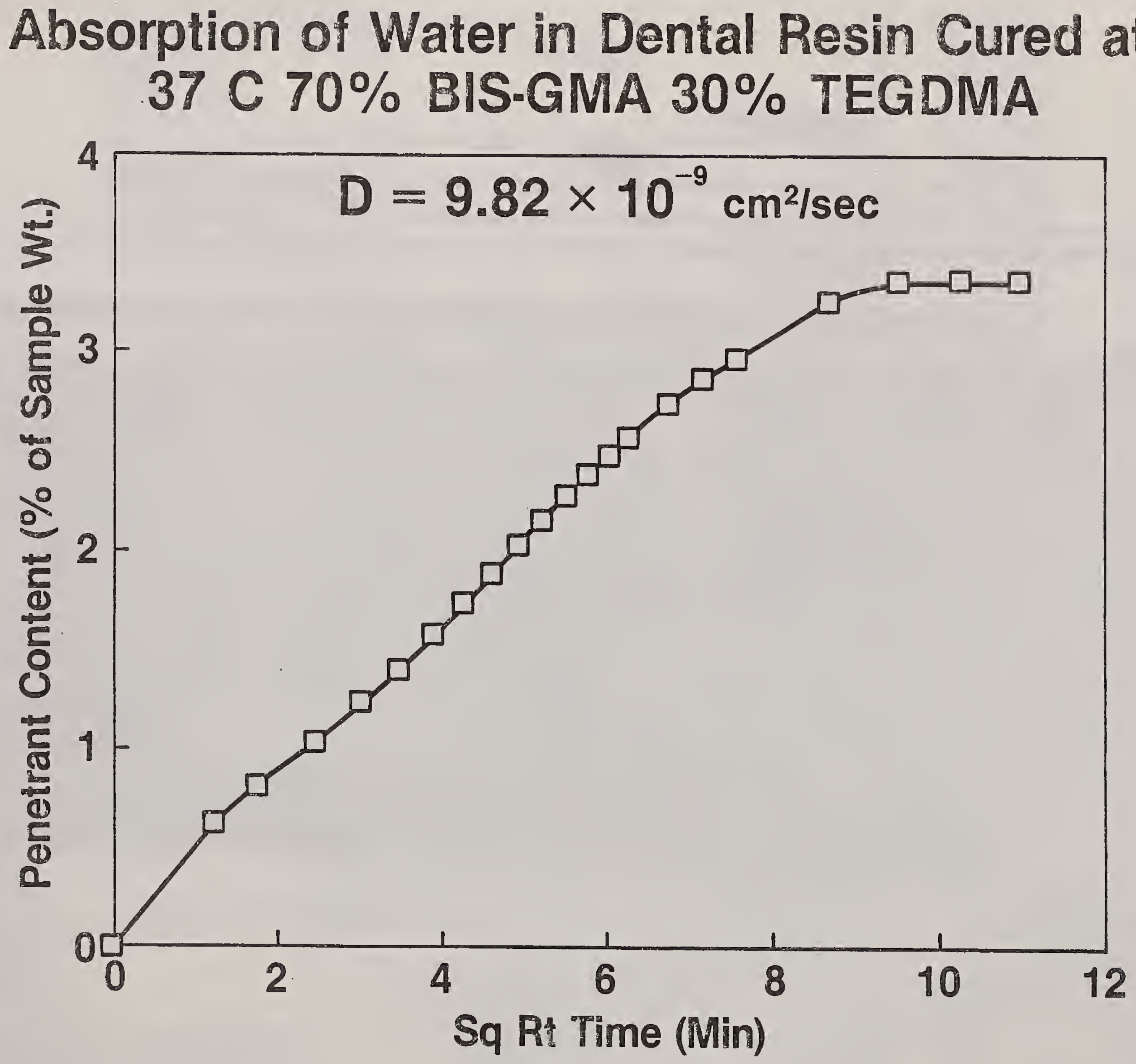


Fig. 9. Absorption isotherm of water into dental resins cured at 37°C (70% BIS-GMA, 30% TEGDMA).

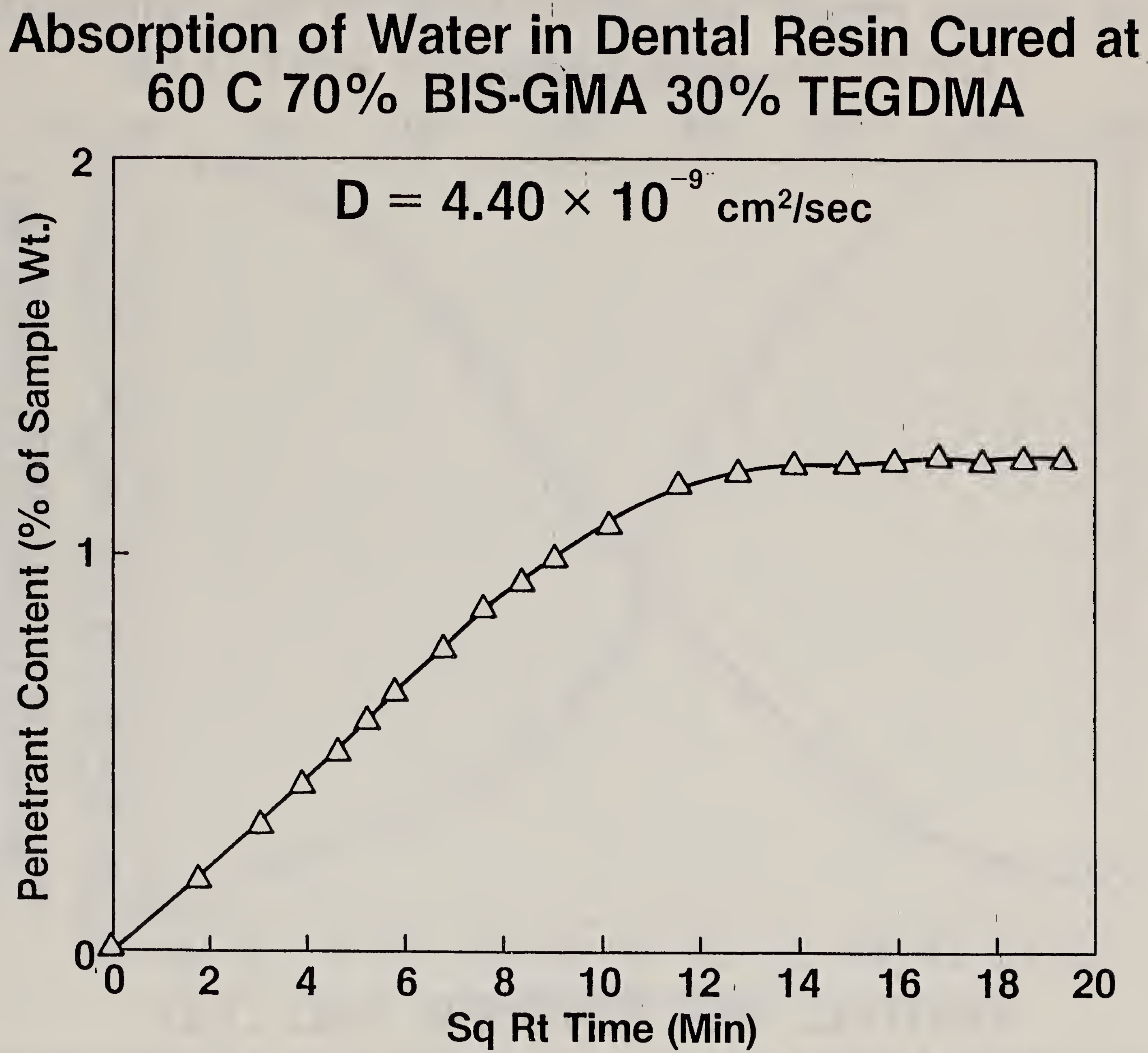


Fig. 10. Absorption isotherm of water into dental resins cured at 60°C (70% BIS-GMA, 30% TEGDMA).

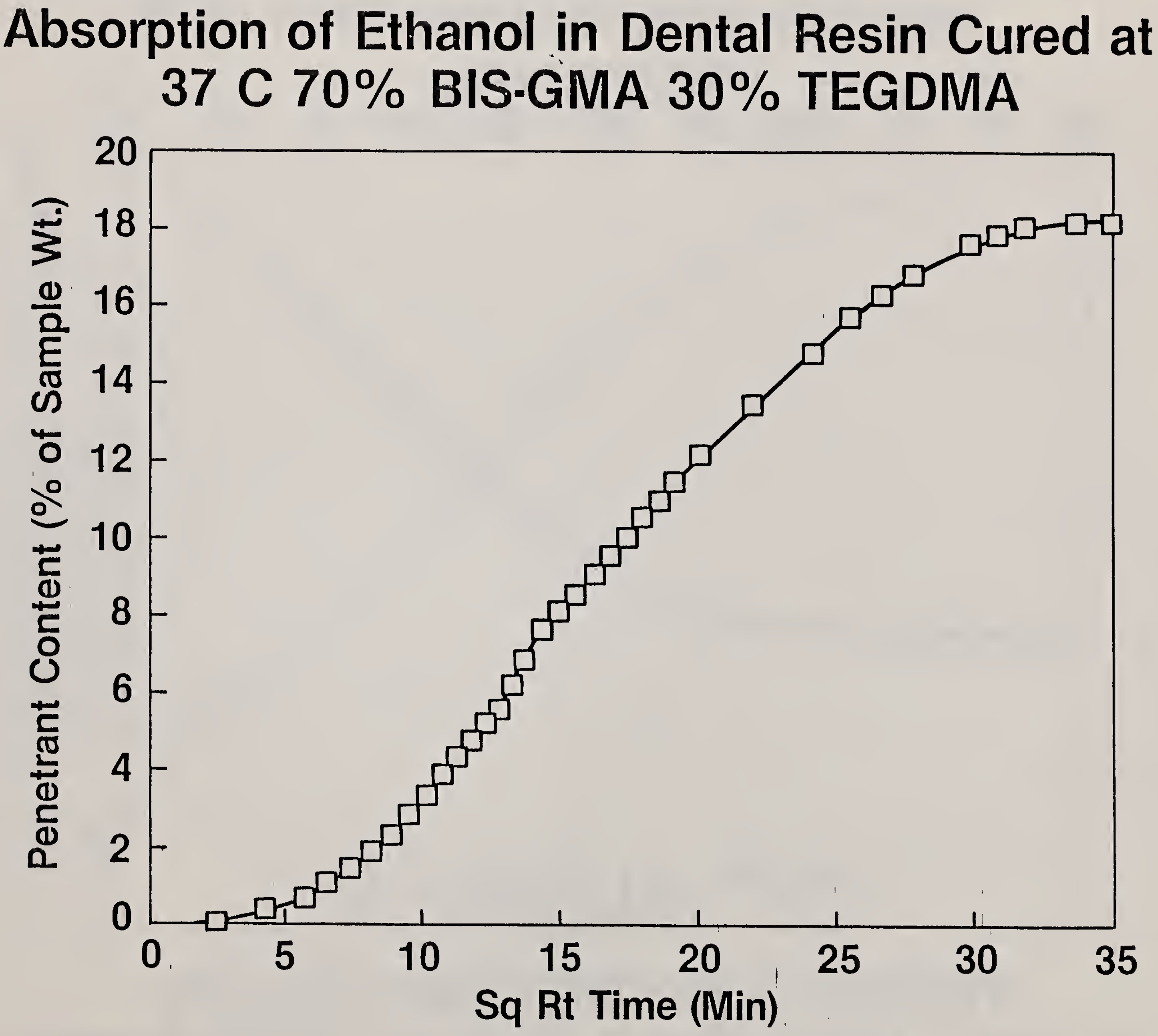


Fig. 11. Absorption isotherm of ethanol into dental resins cured at 37°C (70% BIS-GMA, 30% TEGDMA).

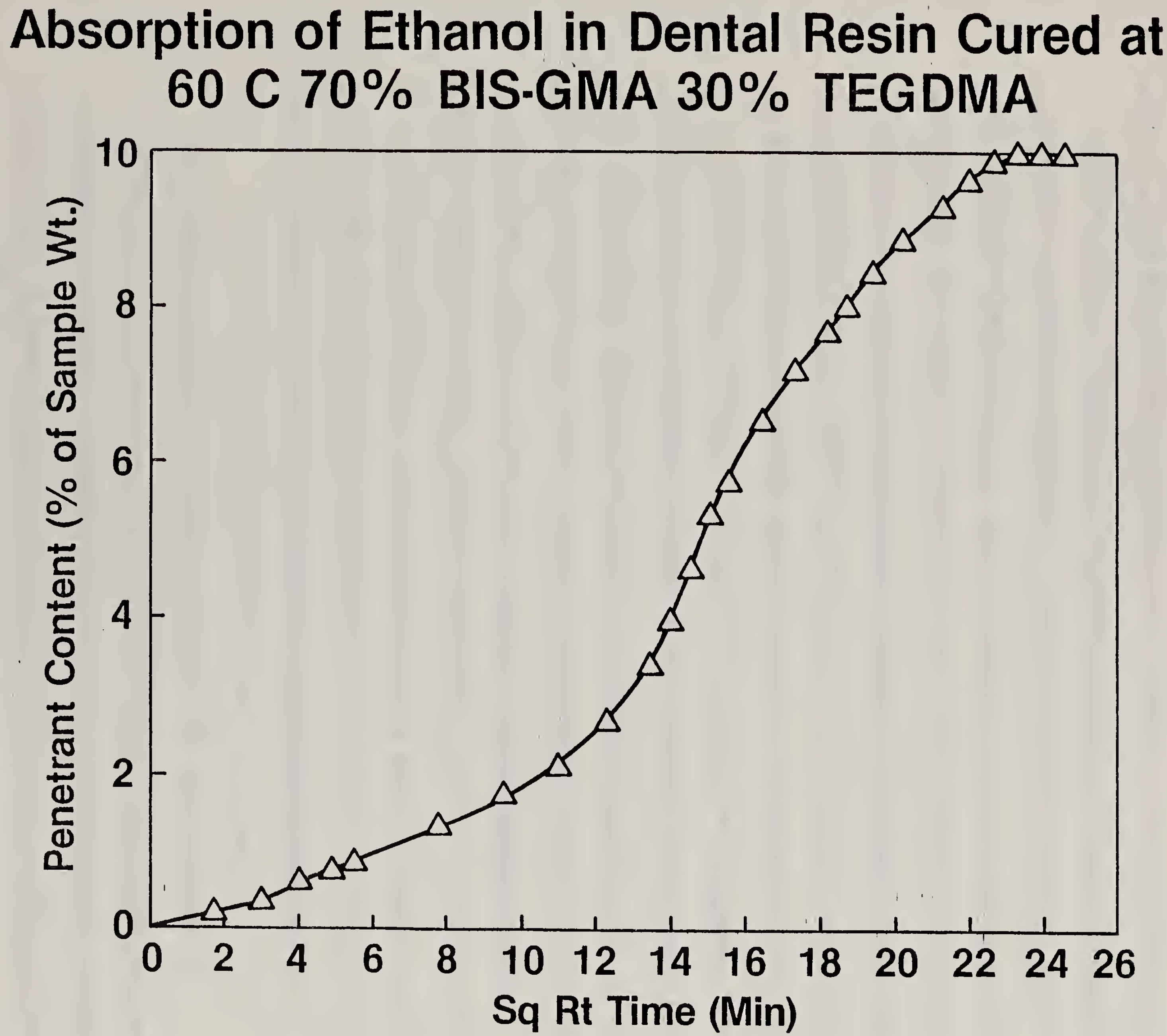


Fig. 12. Absorption isotherm of ethanol into dental resins cured at 60°C (70% BIS-GMA, 30% TEGDMA).

A set of absorption isotherms is shown in figs. 9 thru 12. The specimens were made of 70% BIS-GMA and 30% TEGDMA cured at 37°C and 60°C, respectively. The water absorption process into this dental resin is clearly a Fickian (Class I) type. The values of the amount of water to saturate and the diffusion coefficient are 3.35% and $9.8 \times 10^{-9}$ $cm^2$/sec for the 37°C cured specimens and 1.25% and $4.4 \times 10^{-9}$ $cm^2$/sec for the high temperature cured one. The diffusion process of ethanol into this dental resin is clearly a class II type as demonstrated by the absorption isotherms which indicate saturation values of 18% and 10% for the resins cured at 37°C and 60°C respectively. The physical significance of this type diffusion behavior is twofold: (1) the molecules of the resin are partially dissolved by the penetrant, consequently, the resin changes from a glassy state to a rubbery state. Little wear resistance can be expected with composites composed of a rubbery matrix. This point will be elucidated in a later part of this report. (2) The desorption process of penetrants causing a class II diffusion is abrupt at the very beginning until a hard surface skin is formed. Hereafter, the desorption process is extremely slow with penetrator trapped within the once swollen resin for an extended time. Such slow desorption characteristics of dental resin are likely to be one of the main causes of the subsurface damage layer observed in all the in vivo worn specimens.

### B. Influence of Chemical Softening on Hardness and Wear

As stated in the last section, chemical softening of dental composite restoratives is believed to be very relevant to in vivo durability. Hence, the influence of food simulating chemical solvents on hardness and in vitro wear is being studied. The chemicals used are included in Table 26, along with their solubility parameter values in SI Units and examples of food they simulate. These chemicals include those recommended by FDA CFR 177.2420 (1980) (also see Ref. 41). Although the acetic acid solution is not expected to play a role as a polymer solvent, it is conceivable that this solution may degrade interfacial bonding (between matrix and filler) of some composites.

Three commercial composites, Adaptic, Profile, and Prisma-fil were evaluated. Adaptic was chosen as a conventional type and hence served as a control. Profile is unique in that it employs a strontium glass. Prisma-fil is a current light activated system. The composites were mixed according to the manufacturer's specification and shaped into thin discs suitable for wear tests. After initial curing they were stored in distilled water at 37°C for one day after which they were immersed in each of the solvents included in Table 26 for one week. Although 0.1% acetic acid was included in this study, its solubility parameter value is not included in the Table. We believe that the polymer matrix is not soluble in this chemical as with some of the others. However, there is a possibility that the filler, or interface, may be damaged from extended immersion of the composite in this chemical.

Earlier results of this work were included in the last report [2]. As a consequence of the large specimen-to-specimen variation in the hardness and wear measurements we found it necessary to obtain more data.

### Knoop Hardness Number (KNH) Measurements

During the immersion of the specimens in the various chemicals the Knoop Hardness of these specimens was monitored at 0, 3, and 7 days. The averages taken over five values on each specimen was given in Tables 27, 28, and 29 for Adaptic, Profile, and Prisma-fil. Although these tables contain considerably more detail than usually presented in an annual

## TABLE 26

## Chemicals Used and Solubility Parameter Values*

| Substance | $\delta \times 10^{-4}$ $(J^{1/2}\ m^{-3/2})$ | Examples of Foods Simulated |
|---|---|---|
| Acetic Acid 0.1% | NA | Citrus fruits, vinegar, tomatoes |
| Ethanol in Water: | | |
| 0% | 4.79 | Water, light beverages, alcohol, candy, syrups, wine |
| 25% | 4.24 | |
| 50% | 3.70 | |
| 75% | 3.15 | |
| 100% | 2.60 | |
| Heptane | 1.51 | Vegetable oil, fats |

NA=Not applicable
* Ref. 42

## TABLE 27

## Knoop Hardness of Adaptic as Affected by Solvent Immersion

| | | KNH | | | | |
|---|---|---|---|---|---|---|
| Specimen | Solvent | Day 0 (SD) | Day 3 (SD) | Day 7 (SD) | $P_i/P_f$ | $(P_i/P_f)_{Av}$ |
| 1 | Water | 56.5 (11.4) | 67.9 (11.3*) | 61.1 (7.2**) | 0.92 | |
| 2 | | 92.4 (12.5) | 78.5 (2.2) | 65.4 (1.7) | 1.41 | |
| 3 | | 34.7 (3.4) | 31.5 (1.7) | 29.4 (1.7) | 1.18 | 1.17 |
| 4 | 25% Eth | 87.3 (16.8) | 36.7 (6.0) | 36.4 (3.4) | 2.40 | |
| 5 | | 44.2 (2.9) | 31.5 (3.3) | 23.1 (1.6) | 1.91 | 2.15 |
| 6 | 50% Eth | 57.8 (9.7) | 38.4 (2.7) | 35.6 (6.8) | 1.62 | |
| 7 | | 56.7 (4.8) | 36.2 (4.5) | 18.8 (1.5) | 3.02 | 2.32 |
| 8 | 75% Eth | 70.6 (3.2) | 38.7* | 53.5** | 1.32 | |
| 9 | | 97.4 | 47.7* | 49.6** | 1.96 | |
| 10 | | 59.8 (3.9) | 17.2 (1.5) | 17.6 (1.4) | 3.40 | |
| 11 | | 52.3 (7.6) | 15.5 (0.8) | 15.7 (1.0) | 3.33 | 2.50 |
| 12 | 100% Eth | 51.5 | 82.2* | 45.5** | 1.13 | |
| 13 | | 57.7 (6.2) | 31.1 (4.0) | 19.3 (1.5) | 2.99 | 2.06 |
| 14 | Heptane | 110.9 | 70.0* | 80.1** | 1.38 | |
| 15 | | 78.8 (8.9) | 95.1 (4.4) | 87.0 (7.7) | 0.91 | 1.15 |
| 16 | Acetic Acid(0.1%) | 55.1 (5.5) | 61.8 (5.2) | 64.1 (2.6) | 0.86 | |
| 17 | | 47.3 (2.9) | 48.2 (5.1) | 27.8 (3.1) | 1.70 | |
| 18 | | 63.1 (4.4) | 29.1 (1.9) | 33.1 (2.0) | 1.91 | 1.49 |
| Average | | 65.3 | | | | |
| St.Dev. | | 20.3 | | | | |

* Day 1
** Day 4

# TABLE 28

## Knoop Hardness of Profile as Affected by Solvent Immersion

| | | KNH | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Specimen | Solvent | Day 0 | (SD) | Day 3 | (SD) | Day 7 | (SD) | $P_i/P_f$ | $(P_i/P_f)_{Av}$ |
| 1 | Water | 82.8 | (13.4) | 87.3 | (6.2) | 70.8 | (2.9) | 1.17 | |
| 2 | | 86.3 | (9.5) | 82.6 | (6.9) | 66.1 | (3.1) | 1.31 | |
| 3 | | 48.7 | (3.8) | 49.1 | (3.4) | 44.3 | (4.6) | 1.11 | |
| 4 | | 30.1 | (1.5) | 27.9 | (1.8) | 26.0 | (1.4) | 1.16 | 1.19 |
| 5 | 25% Eth | 71.7 | (4.6) | 38.8 | (6.3) | 42.1 | (4.9) | 1.70 | |
| 6 | | 42.8 | (6.1) | 24.3 | (2.2) | 24.4 | (3.6) | 1.76 | |
| 7 | | 40.3 | (3.4) | 27.5 | (1.9) | 26.8 | (2.5) | 1.50 | 1.65 |
| 8 | 50% Eth | 48.8 | (5.8) | 33.3 | (5.6) | 33.2 | (3.7) | 1.47 | |
| 9 | | 63.3 | (7.1) | 38.3 | (3.3) | 27.7 | (2.8) | 2.29 | |
| 10 | | 46.2 | (4.1) | 21.6 | (2.2) | 20.1 | (0.6) | 2.30 | |
| 11 | | 58.9 | (4.3) | 32.1 | (1.0) | 26.0 | (5.4) | 2.27 | 2.08 |
| 12 | 75% Eth | 62.0 | (5.6) | 38.4* | | 42.0** | | 1.48 | |
| 13 | | 86.9 | | 40.4* | | 52.0** | | 1.67 | |
| 14 | | 53.0 | (3.1) | 19.7 | (2.8) | 19.6 | (2.4) | 2.70 | |
| 15 | | 44.3 | (4.1) | 22.8 | (3.7) | 16.7 | (1.6) | 2.65 | |
| 16 | | 54.5 | (4.4) | 26.5 | (0.9) | 19.3 | (1.8) | 2.82 | 2.26 |
| 17 | 100% Eth | 51.4 | | 42.4* | | 43.1** | | 1.19 | |
| 18 | | 51.6 | (3.4) | 36.1 | (3.2) | 18.6 | (1.9) | 2.77 | |
| 19 | | 55.5 | (2.0) | 34.9 | (3.7) | 31.4 | (1.6) | 1.77 | 1.91 |
| 20 | Heptane | 72.9 | | 90.3* | | 113.4** | | 0.64 | |
| 21 | | 79.4 | (5.2) | 77.3 | (7.0) | 83.6 | (9.5) | 0.95 | 0.79 |
| 22 | Acetic | 68.0 | (4.5) | 45.6 | (4.1) | 38.4 | (1.0) | 1.77 | |
| 23 | Acid(0.1%) | 52.7 | (3.3) | 41.5 | (3.3) | 18.8 | (1.0) | 2.80 | |
| 24 | | 48.8 | (2.7) | 22.2 | (2.7) | 22.1 | (1.9) | 2.21 | 2.25 |
| Average | | 58.4 | | | | | | | |
| St, Dev. | | 15.2 | | | | | | | |

* Day 1
** Day 4

## TABLE 29

## Knoop Hardness of Prisma Fil as Affected by Solvent Immersion

| | | KNH | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Specimen | Solvent | Day 0 | (SD) | Day 3 | (SD) | Day 7 | (SD) | $P_i/P_f$ | $(P_i/P_f)_{Av}$ |
| 1 | Water | 53.8 | (5.6) | 52.6 | (2.2) | 54.4 | (4.9) | 0.99 | |
| 2 | | 88.3 | (9.8) | 82.9 | (3.1) | 65.5 | (2.2) | 1.35 | |
| 3 | | 30.8 | (4.7) | 30.0 | (2.8) | 28.7 | (1.0) | 1.07 | 1.14 |
| 4 | 25% Eth | 51.7 | (2.8) | 36.3 | (2.7) | 37.3 | (1.6) | 1.39 | |
| 5 | | 32.8 | (0.7) | 28.9 | (0.9) | 25.1 | (0.7) | 1.31 | 1.35 |
| 6 | 50% Eth | 50.2 | (2.0) | 31.7 | (2.9) | 29.7 | (0.9) | 1.69 | |
| 7 | | 48.8 | (1.3) | 34.5 | (1.4) | 29.0 | (0.8) | 1.68 | 1.69 |
| 8 | 75% Eth | 58.6 | (3.3) | 28.7* | | 37.7** | | 1.55 | |
| 9 | | 57.6 | | 40.2* | | 38.2** | | 1.51 | |
| 10 | | 43.5 | (2.7) | 18.7 | (1.7) | 17.2 | (0.8) | 2.53 | |
| 11 | | 37.5 | (2.3) | 22.2 | (1.2) | 25.5 | (1.0) | 1.47 | 1.77 |
| 12 | 100% Eth | 45.0 | | 40.2* | | 37.4** | | 1.20 | |
| 13 | | 49.4 | (1.7) | 32.6 | (1.5) | 31.5 | (1.3) | 1.57 | 1.39 |
| 14 | Heptane | 64.6 | | 67.3* | | 72.0** | | 0.90 | |
| 15 | | 59.0 | (2.3) | 59.8 | (3.3) | 52.7 | (3.0) | 1.12 | 1.01 |
| 16 | Acetic | 48.7 | (1.5) | 42.5 | (1.6) | 36.4 | (7.9) | 1.34 | |
| 17 | Acid(0.1%) | 40.2 | (0.7) | 35.6 | (1.1) | 28.0 | (2.8) | 1.44 | |
| 18 | | 37.3 | (1.2) | 33.6 | (1.1) | 26.7 | (1.3) | 1.40 | 1.39 |
| Average | | 49.0 | | | | | | | |
| St.Dev. | | 13.4 | | | | | | | |

* Day 2

** Day 4

report, they are included here to portray the difficulties in obtaining reliable KNH values on composites. In the tables the numbers to the right of each of the KNH values are the standard deviations obtained from five measurements at different positions on each specimen. $p_i/p_f$ is the ratio of the initial hardness value (day 0) to the final day (day 7). This ratio is taken to be a measure of chemical softening. The hardness ratios are followed by their average values for each chemical. Ideally all of the KHN values for each composite at day 0 should be identical, since these measurements were obtained before immersion in the chemicals. The average KHN (day 0) value is given at the bottom of each table. The accompanying large standard deviation represents both specimen to specimen variation and that within each specimen. In Fig. 13, $p_i/p_f$, which is a measure of chemical softening, is plotted against the solubility parameters of the chemical solvents. The ethanol concentrations and H=heptane are indicated as parameters. Although acetic acid is not included here for the reason given above, it produces a significant degree of softening on all composites. In the figure the largest effect is seen on Adaptic, and the least, on Prisma-fil. The hardness ratios reach a maximum at about $\delta = 3.15 \times 10^{-4}\ J^{1/2}m^{-3/2}$ which corresponds to an ethanol concentration of 75%. We believe that this value of $\delta$ approximates that for BIS-GMA.

### 1. Wear Measurements on Chemically Soaked Composites

The pin and disc wear apparatus [6, 43] is completely automated comprising three identical rotating platforms containing the disc shaped specimens of the material to be investigated. A stationary slider (pin) of stainless steel, type 303, impinges on each of the rotating specimens producing a wear track of 12 mm mean diameter. Stainless steel pins are

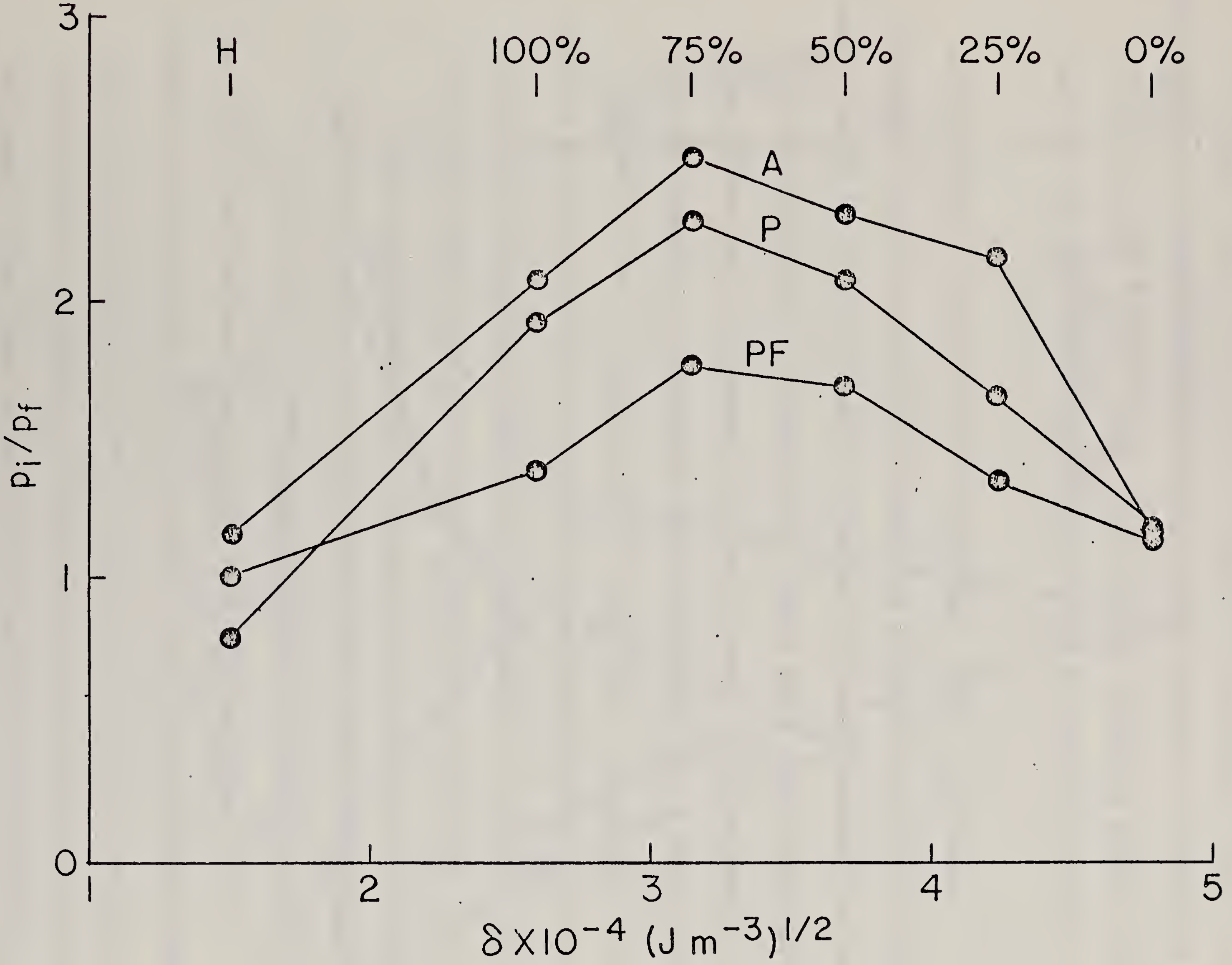


Fig. 13. Hardness ratio, $p_i/p_f$, plotted against solubility parameter, $\delta$, for three composites.

used because they produce subsurface damage similar to that observed on *in vivo* worn restorations [44]. 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.

Immediately after completion of the chemical soaking period, pin and disc wear measurements were taken on the three classes of specimens. The wear measurements comprise two parts. The first is a set of measurements for which the average track depth (from a set of 10 values around the track circumference) is taken at each of 5 sequential disc revolutions. The track depth at the end of the fifth revolution is referred to here as the initial wear, $\underline{s}$. Reliable initial wear data is very difficult to obtain because of the requirement that pin and disc surfaces must be very smooth and parallel. Subsequently track depth measurements were taken every hour for 30 hours where each hour corresponds to about 1500 cycles. In most cases for which the wear was apparently linear with time (or track length) the steady state wear rate $m_s = ds/dt$, where $\underline{s}$ is the track depth, was evaluated by a linear regression.

Since we do not have wear data on each specimen before immersion, we cannot treat the results in a manner parallel to that for the hardness employing the ratio $p_i/p_f$. In figure 14 the initial wear for the three composites is plotted against the solubility parameter of the solvents. The trends are similar to those of $p_i/p_f$ shown in figure 13, except the

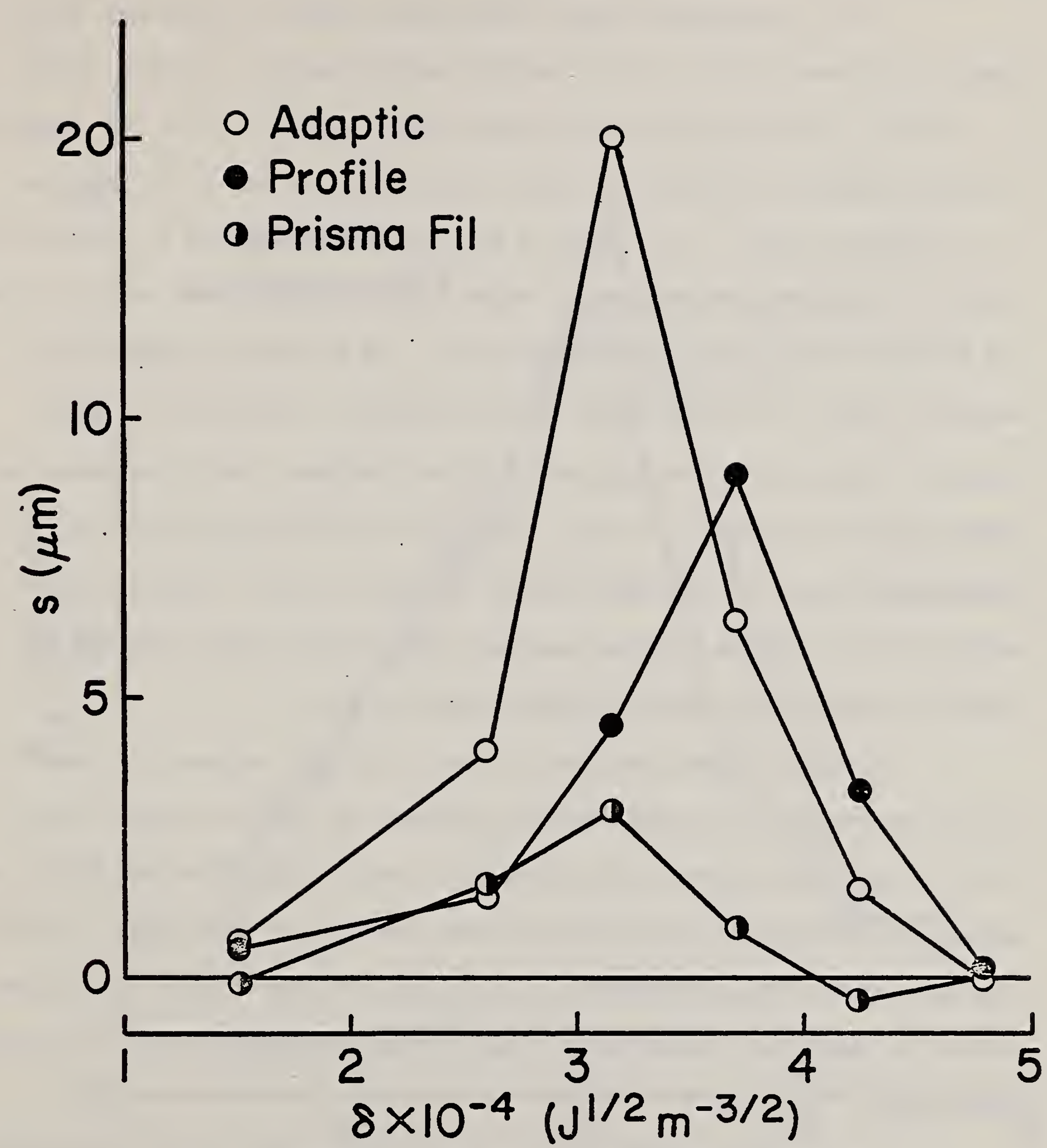


Fig. 14. Initial wear s plotted against solubility parameter, δ, for three composites.

values of s for Profile tend to maximize at the larger value δ which corresponds to a 59% ethanol solution.

The corresponding steady state wear rates, $m_s$, obtained subsequently are shown in fig. 15 for Adaptic and Prisma Fil. At most values of δ there is little distinction between the $m_s$ values of the two composites. The wear behavior of Profile is more complicated and had to be analyzed in a different manner. In figure 16 the wear track depth s is plotted against time for a specimen preimmersed in water at 37°C for one week and for a specimen stored in air at the same temperature. The distinction between the amounts of wear in the two cases is considerable. Also note the large extent of nonlinearity for the water soaked specimen. With the other two composites the response is linear, and there is little or no distinction between wear rates of specimens stored in water or air. The value $m_s = 0.86$ μm/h of the air stored Profile specimen approximates those obtained for the other two composites stored in either water or air.

A plausible explanation for the difference between the amounts of wear of water and air-stored Profile specimens is that the glass filler or sanilizer used may undergo some hydrolysis when stored in water. This could weaken the interfacial bonding manifested by a larger wear rate. Possible explanations for the nonlinear wear observed for water stored Profile are decreasing penetrant concentration and/or time for damage infliction decreasing with depth.

The general wear behavior of dental composites (except for Profile and possibly others affected by water) may be summarized as depicted schematically by figure 17. As indicated in the figure the initial wear may be severe. As much as 180 μm of material has been removed over the first five revolutions. This high wear rate is attributed to the removal of a

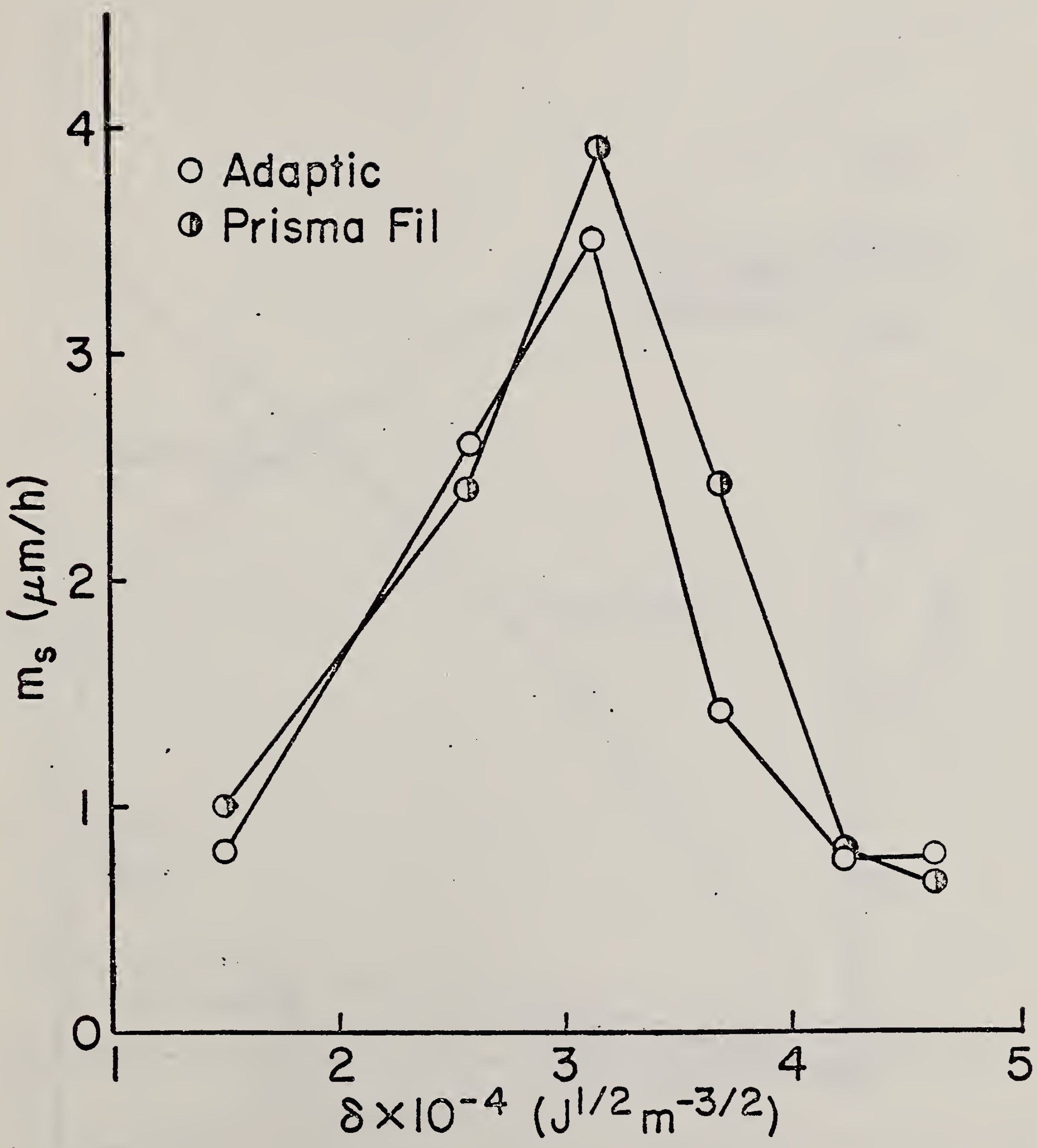


Fig. 15. Steady state wear, $m_s$. plotted against solubility parameter, δ, for three composites.

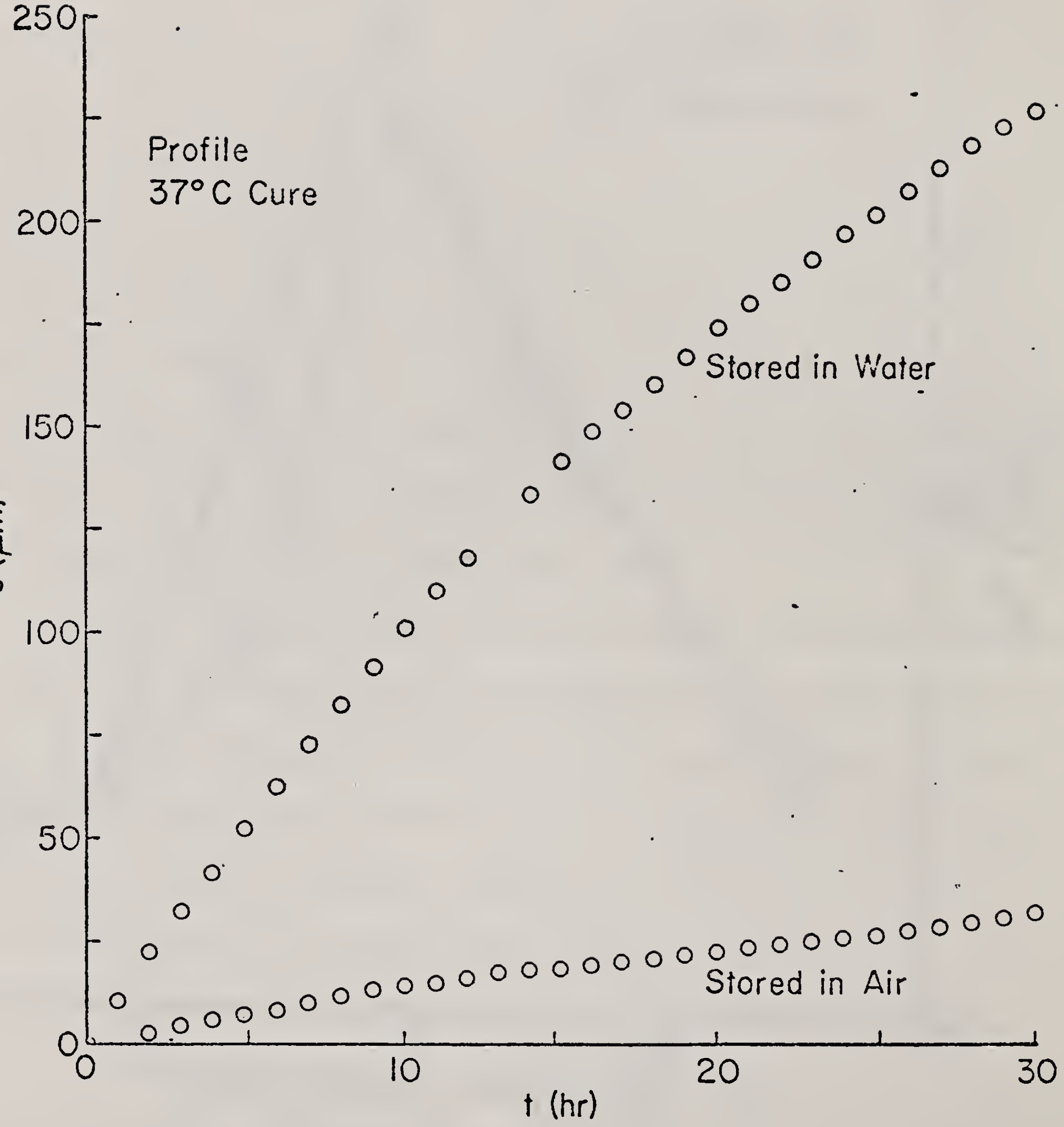


Fig. 16. Wear track depth, s, of Profile with time for specimens stored in air and water prior to tests.

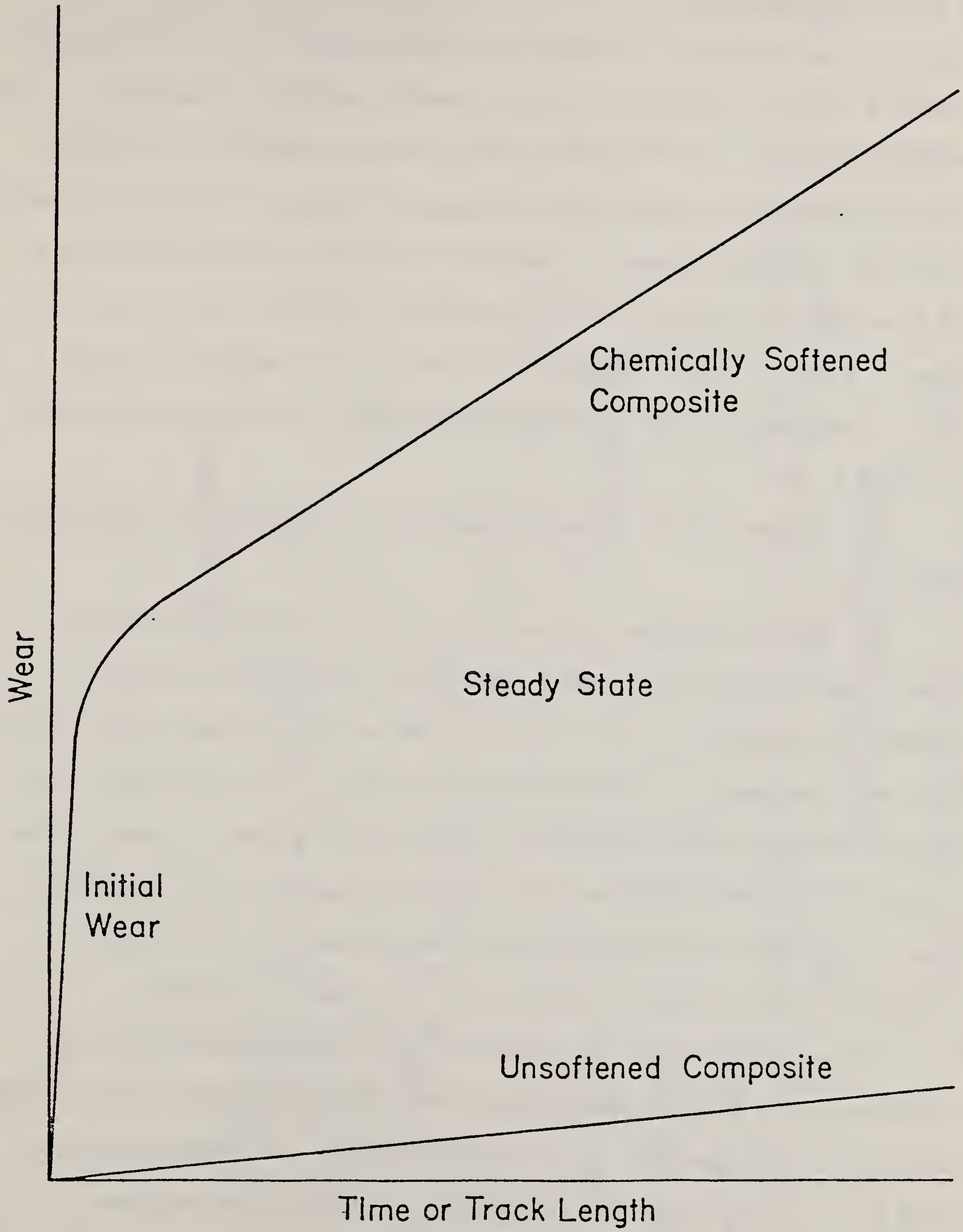


Fig. 17. Schematic comparison between the wear of a chemically softened and unsoftened composite.

a severely damaged layer induced by the solvent. After this surface layer is removed the wear reaches an apparent steady state, which approximates 3 m/h at 1550 rev/h; with for example, Adaptic preimmersed in a 75% ethanol solution. In the steady state region the composite is softened by the diffusion of solvent, but no damage is apparent from the microdefect analyses. Beyond one week of immersion the solvent may penetrate 200 μm of material. The removal of this amount would require nearly 3 days of wear at 3 μm/h. After this period the wear rate is expected to reach that corresponding to the unsoftened composite. For Adaptic this value is about 1 μm/h.

### C. Degree of Cure in Dental Composites as Function of Cure Temperature and Time

The extent of polymerization as depicted by the residual double bond concentration of the dental composites cured at 37°C has been assumed to be relatively low. This low degree of the double bond conversion may be a consequence of either the high viscosity of the partially cured macromolecules or the unsatisfactory performance of the initiators. The purpose of the work described in the following section is to determine the factors which limit the degree of polymerization of the dental composites and result in a vulnerability to chemical softening.

The concentration of the unreacted double bond concentration was measured with a Fourier Transform Infrared (FTIR) technique. The specimens were thin films cured for up to seven days under conditions of 37°C and 100% RH. The specimens were exposed to room temperature and lower humidity only during the IR measurements which required one minute on the average. The results of these FTIR measurements are summarized in figure 18. The most striking feature of the results is that the degree

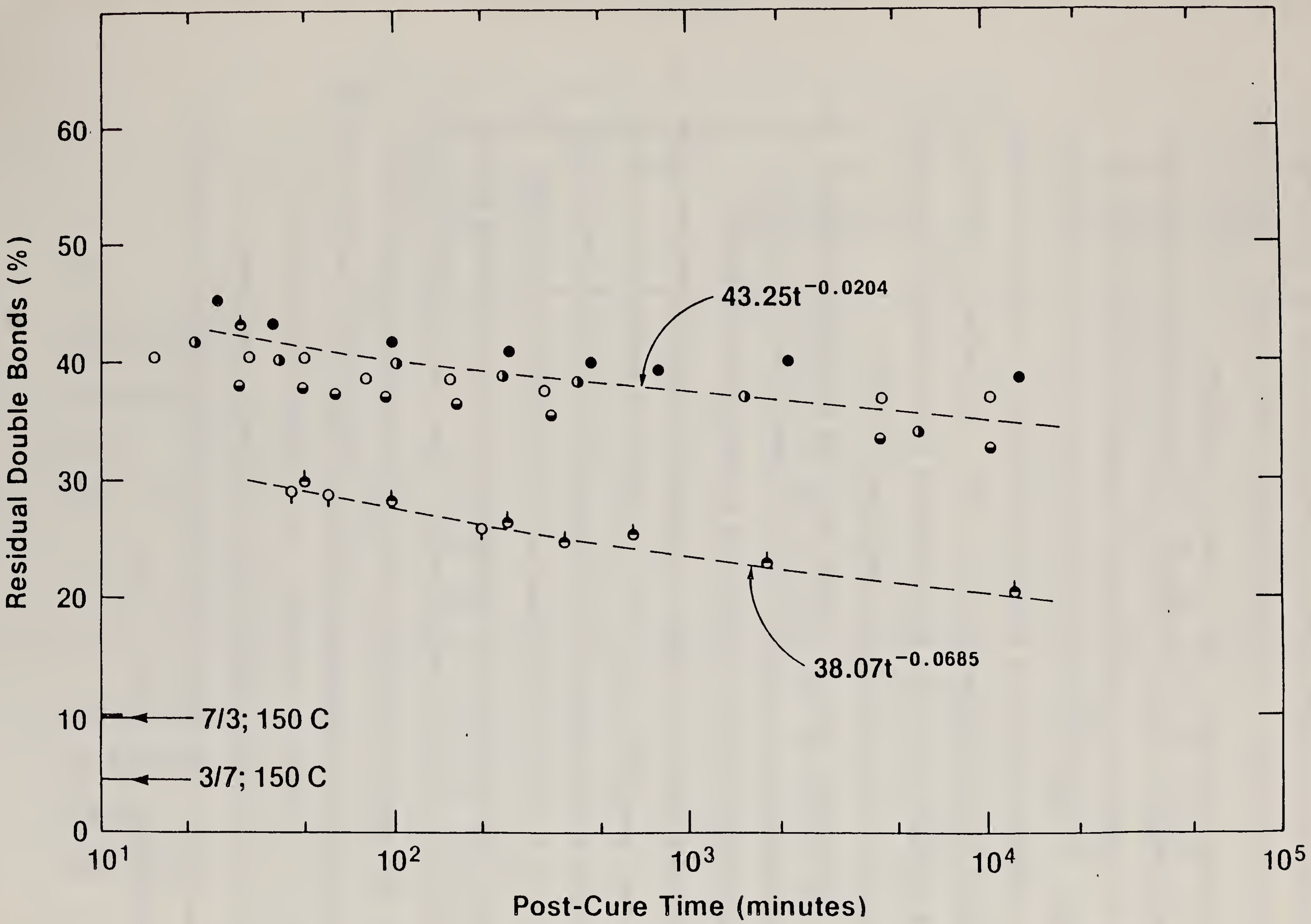


Fig. 18. Post-curing of BIS-GMA copolymers kept at 37°C, 100% RH: ◑...BIS-GMA (70), TEGDMA (30), 1% BPO; ○...BIS-GMA (70), TEGDMA (30), 2% BPO; ●, ◒...BIS-GMA (70), TEGDMA (30), 2% Cumene HPO; δ, ϙ...BIS-GMA (30), TEGDMA (70), 1% BPO.

of polymerization depends essentially on the viscosity of the monomer or the resultant polymer. The concentration of the initiator and the type of initiator have only a minor effect on the degree of curing once an adequate amount is used. Furthermore, the copolymer with 70% BIS-GMA and 30% TEGDMA has a limited extent of postcuring after the first 30 minutes. Extrapolation at 37°C/100% RH data to one year yields double bond concentrations far in excess of that obtained by curing the same system at elevated temperature, i.e. 150°C. The monomer system with 7/3 BIS-G MA/TEGDMA will still have 36% double bond unreacted after one year versus 10% left for the same polymer cured at 150°C.

The degree of cure of a dental resin can be improved by raising the curing temperature as shown in fig. 19; however, the time interval between mixing the resin to start the polymerization and heating needs to be kept at a minimum. A subsequent heating of specimens cured at lower temperature, e.g. 37°C, can improve the degree of cure only to a limited extent depending on the elapsed time. Table 30 demonstrates this with an unfilled resin composed of 70% BIS-GMA and 30% TEGDMA. The amount of post-curing due to subsequent heating was calculated from the exothermal peak area of the DSC result. These results clearly indicate that heat needs to be applied to the dental composite directly after mixing to achieve a high degree of cure. However, this immediate heating process is clinically unfavorable. This suggests a new direction for improving the current dental composition, namely, development of a composite that can be post-cured to high completion within a broad time interval after the initial curing.

## Table 30

Additional Polymerization During DSC Scan (296-450°K)
of BIS-GMA Resins Cured and Conditioned at 37°C, 100 RH

| | Elapsed Time (min) | Polymerization Peak Temp.(°C) | Additional Degree of Polymerization |
|---|---|---|---|
| BIS-GMA (70%) | 5 | 42 | 43.71 |
| TEGDMA (30%) | 25 | 72 | 7.17 |
| BPO 1% | 40 | 77 | 7.31 |
| DHPPT 0.5% | 85 | 87 | 2.10 |
| | 180 | 92 | 1.10 |
| | 360 | 99 | 1.29 |
| BIS-GMA (70%) | 5 | 47 | 41.6 |
| TEGDMA (30%) | 30 | 67 | 7.10 |
| BPO 2% | 60 | 72 | 4.90 |
| DHPPT 0.5% | 180 | 77 | 3.10 |
| | 360 | 77 | 2.00 |

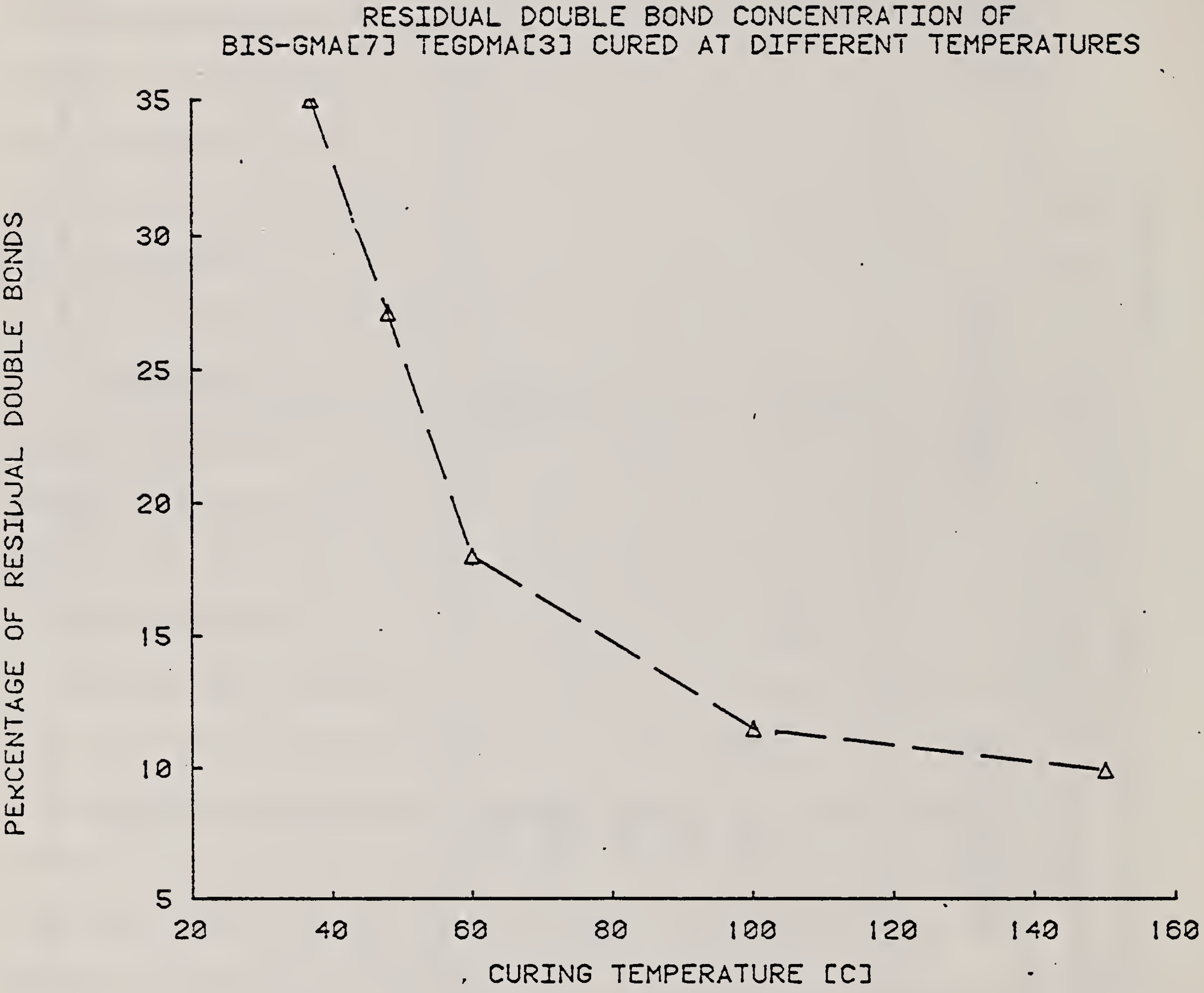


Fig. 19. Residual double bond concentration of 7/3 BIS-GMA/TEGDMA cured at different temperatures.

## D. Influence of Degree of Cure on Hardness and Wear

As stated earlier in this report, chemical softening by food simulating liquids plays an important role on hardness and subsequent wear. It was assumed that chemical softening could be reduced by increasing the extent of crosslinking, or polymerization, which may be accomplished by increasing the cure temperature. Although elevating the cure temperature is not practical for <u>in situ</u> restorations, the resulting information is expected to give valuable insight on the nature of these degradation mechanisms.

Data were obtained on three commercial composites: Adaptic (macrofilled), Silar (microfilled) and Prisma Fil (visible light activated). Specimens were cured isothermally at three temperatures: 37, 60 and 80°C. For the chemically cured composites curing was initiated immediately after mixing. With Prisma Fil, the specimens were allowed to reach thermal equilibrium at the cure temperatures before the light source was applied. After curing, the specimens were soaked in distilled water and 75% ethanol-25% water solution at 37°C for one week prior to tests. The 75% ethanol solution was chosen because it produced the most damage on all composites investigated here as shown earlier in this report.

In figure 20 the hardness ratio, $p_i/p_f$ is plotted against the cure temperature $T_c$ for the three composites. The upper set comprising data for the three specimens cured at three temperatures pertains to pre-immersion in the 75% ethanol solution. Except at 37°C the extent of softening (measured by $p_i/p_f$) is about the same for the three composites, and the softening decreases with increasing $T_c$. With the water soaked specimens a slight amount of softening is apparent. The reason for the apparent increase of $p_i/p_f$ between 37 and 60°C for Silar is not understood

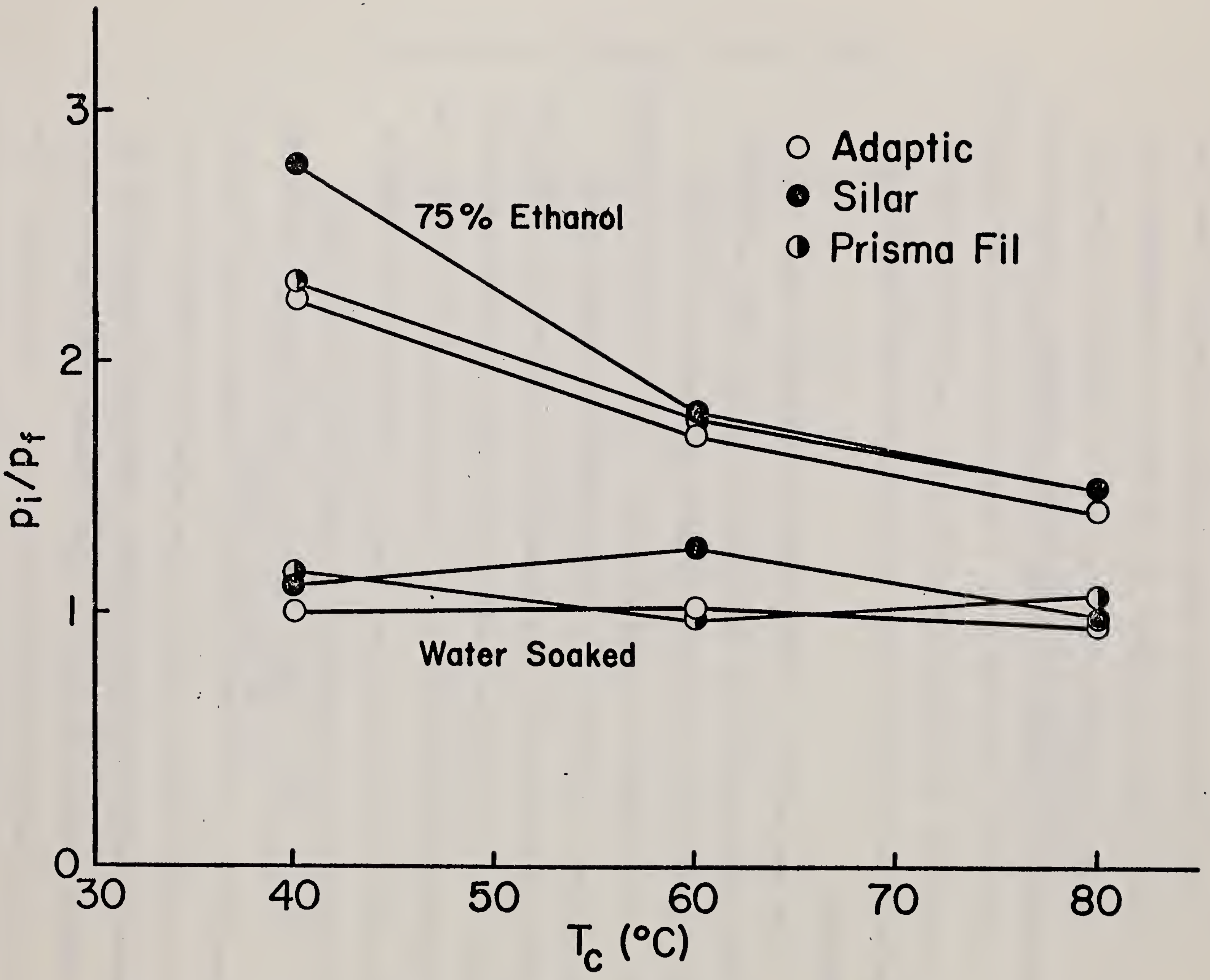


Fig. 20. Hardness ratio, $p_i/p_f$, plotted against cure temperature, $T_c$, for three composites.

unless it is attributed to the imprecision $\Delta p/p \sim 30\%$ based on standard deviation.

The initial wear over five revolutions is depicted on figure 21. All data pertain to the 75% ethanol soaked specimens. In all cases the initial wear essentially vanished at $T_c = 80°C$. With Prisma Fil the initial wear is insignificant except at $T_c = 37°C$. The most dramatic result was obtained on Silar for which the wear changed from about 180 to 0 μm from $T_c = 37$ to 60°C. This result indicates that this composite is very vulnerable to chemical attack when cured <u>in situ</u>; however, this deficiency may be removed by curing at 60°C. The initial wear on the water soaked specimens is not shown because it was insignificant.

The corresponding steady state wear rates are shown in figure 22. Except for one case, the value of $m_s$ decreases with increasing $T_c$. Why the rate for Silar is essentially constant between 37 and 60°C is not understood. This is the region where the corresponding initial wear decreased dramatically.

As stated earlier the initial wear pertains to the removal of an extensively damaged surface layer. The damage is visible through the silver staining microdefect analysis, which reveals the removal of polymer matrix. The steady state wear is accelerated from preimmersion of the specimen in an appropriate solvent. The damage which is apparent from the accelerated rate is not visible from the microdefect analysis. In both cases the extent of damage is decreased by increasing the cure temperature. This produces a more durable material as seen from the increase in hardness and wear resistance of the composites even when they are preimmersed in the solvent.

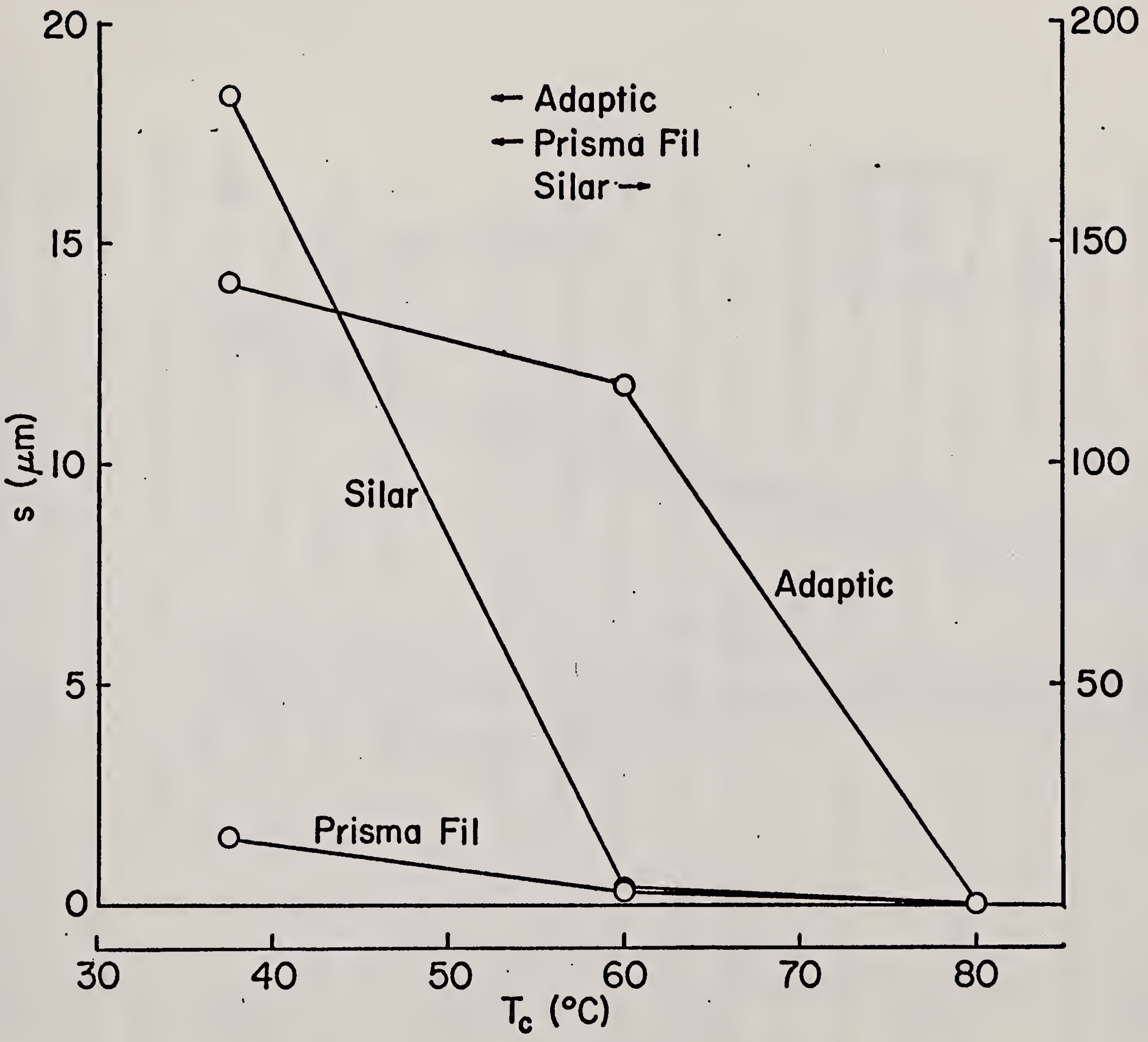


Fig. 21. Initial wear, s, plotted against cure temperature, $T_c$, for composites.

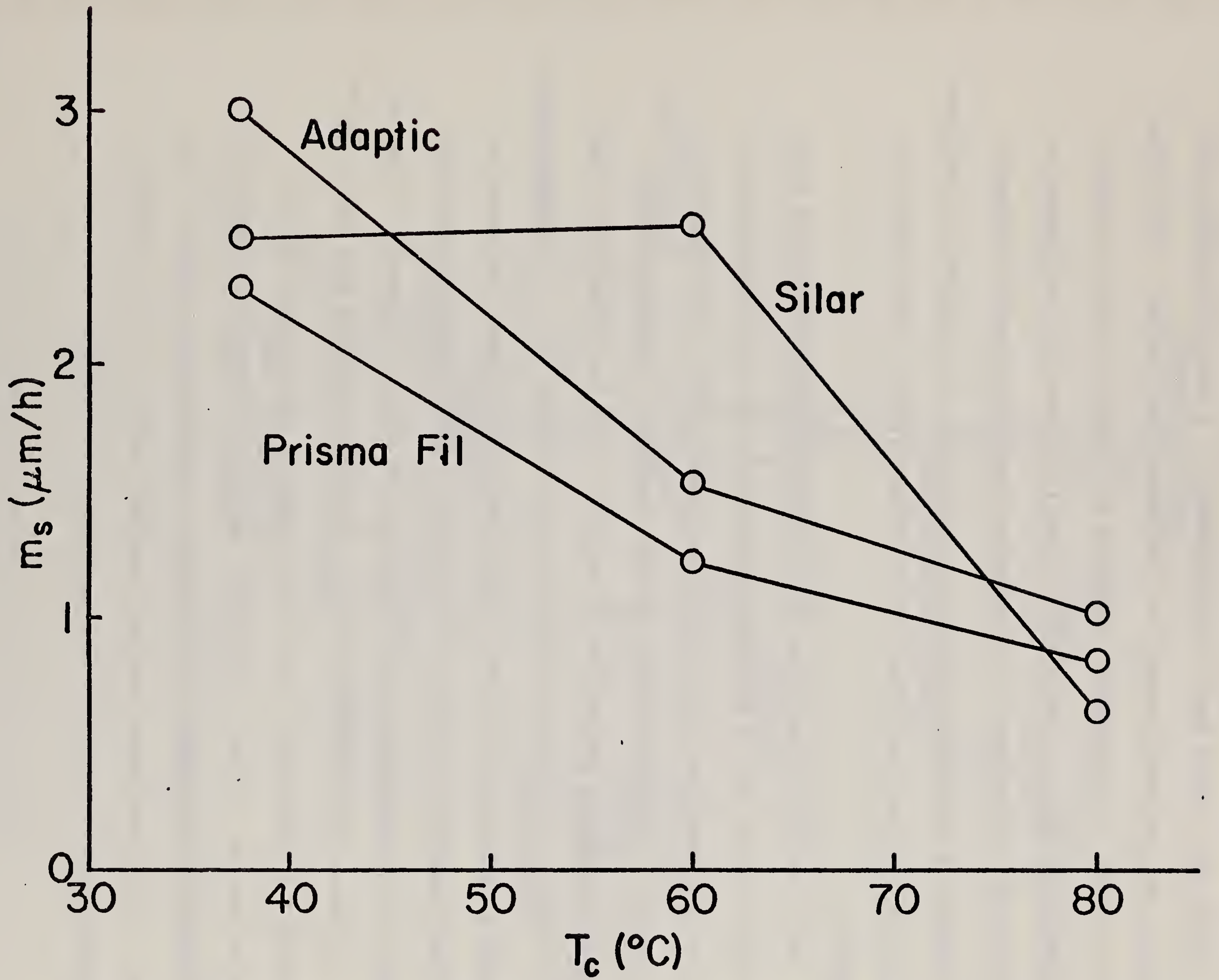


Fig. 22. Steady state wear, $m_s$. plotted against cure temperature, $T_c$, for three composites.

### E. Erosion Tester

During this fiscal year the development of a new test procedure was initiated and completed, except for the temperature control. The purpose of this effort is to obtain an expedient and reliable test to evaluate the erosion of composite restoratives resulting from the impingement of high velocity liquid jets of various food simulating chemical solvents. With composite restorative materials, this device was expected to compliment the pin on disc wear apparatus, which is operationally complicated and expensive.

The principle of operation of the erosion tester is depicted schematically in fig. 23. A pressure approximating 46 psi is generated by a pump which forces the liquid through a tapered nozzle. The resulting jet, which is constant velocity and non divergent, impinges upon the restoration causing the erosion of material. The food simulating liquid is collected at the bottom of the container after which it circulates through a temperature bath and finally back to the pump. The amount of erosion, measured by material loss, is to be determined by weighing the tooth (with restoration), or the specimen and cup, at appropriate intervals.

In the original concept of this device the amount of wear was to be determined by the weight loss of the composite specimen during the erosion process. Using a 75% ethanol solution no detectable weight loss was observed on an Adaptic specimen after testing over a period of one week. It is conceivable that any detectable weight loss is counterbalanced by the absorption of solvent into the specimen.

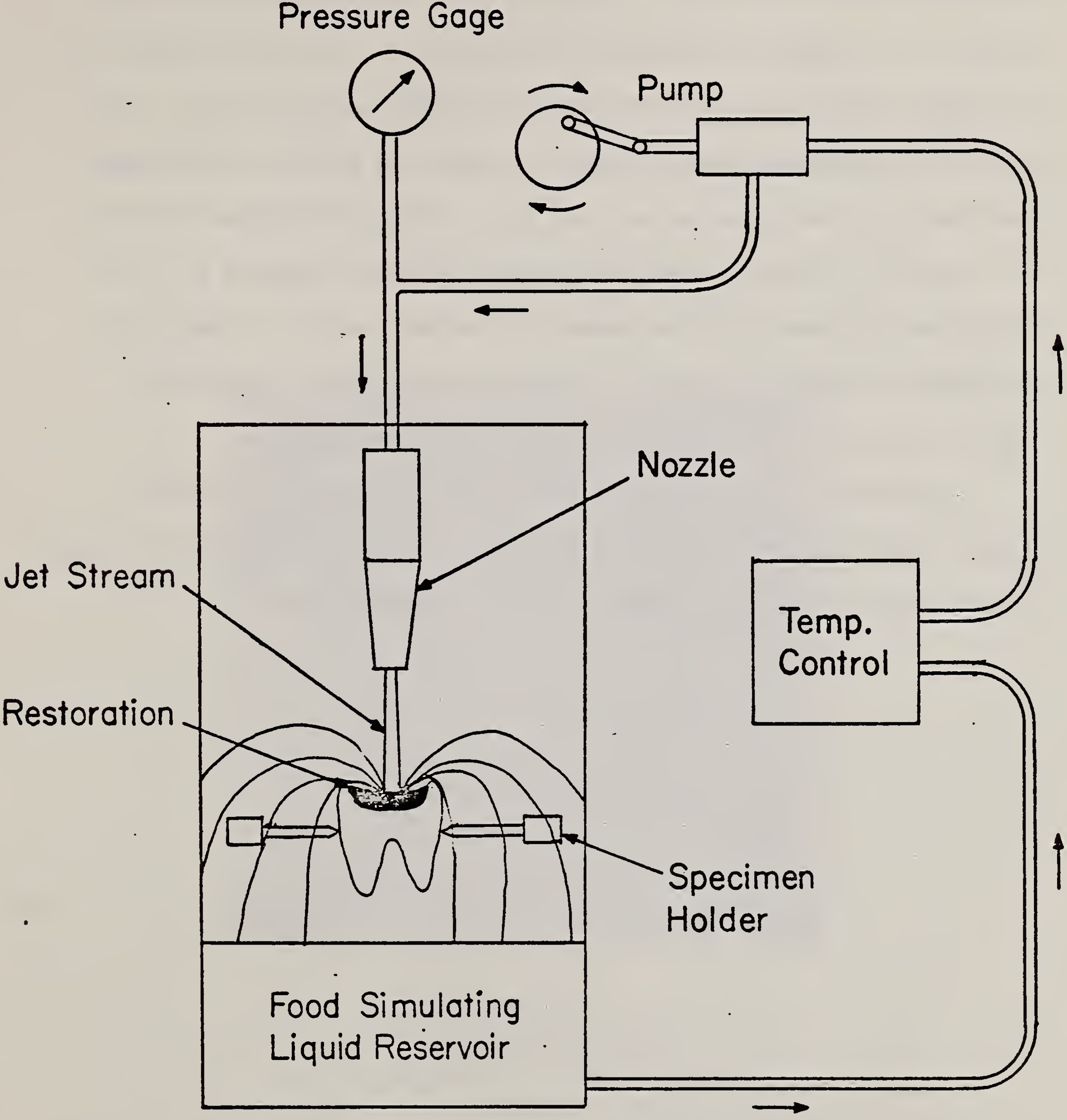


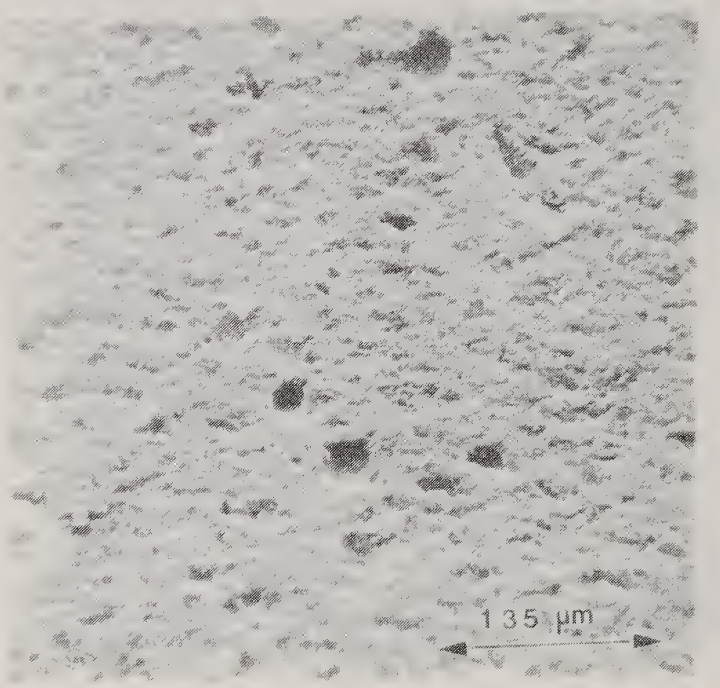
Fig. 23. Schematic drawing of the erosion tester.

From electron scanning microscopy some damage is apparent over extended periods of erosion. Figure 24 is a micrograph showing the surface of an Adaptic specimen prior to tests. The surface appears to be smooth except for voids and faint horizontal cutting marks. Using about the same magnification figure 25 shows the surface at the same specimen after being subjected to a 46 psi jet of 75% ethanol solution for 6 days. The rough appearance results from the exposure of filler particles laid bear from the removal of polymer matrix. Figure 26 is eqivalent to figure 25 except at higher magnification. Using this magnification the filler particles are clearly visible.

In future work an effort will be made to quantify the erosion tester, possibly by producing more severe erosion in order that a significant weight loss may be detected over a reasonable time.

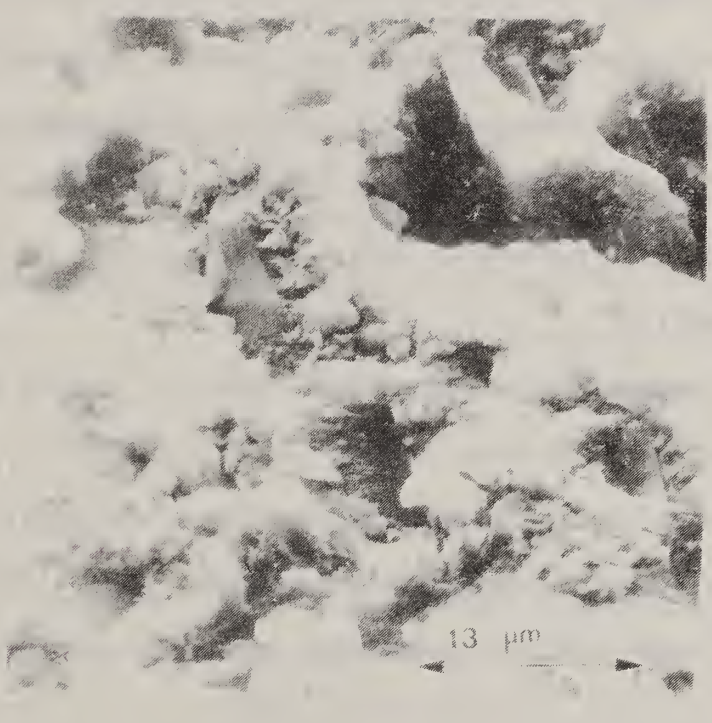
Specimen 8b
Control (Adaptic)

Fig. 24. Micrograph of the surface of an uneroded specimen of Adaptic.



Specimen 8a - Erosion Tested
with 75% Ethanol - 6 days;
Jet Pressure 46 PSi
(Adaptic)

Fig. 25. Micrograph of the surface of a specimen of Adaptic eroded by a 75% ethanol solution for 6 days.



Specimen 8a - Erosion Tested
with 75% Ethanol - 6 days;
Jet Pressure 46 PSi
(Adaptic)

Fig. 26. Micrograph of the surface shown in figure 25 but at higher magnification.

## III. Dental Alloys and Ceramics

The continually changing economic conditions, both domestic and foreign, have resulted in steady interest in new dental alloy and ceramic products which are less expensive or more price-stable, supply stable and of satisfactorily predictable performance. The latter requires the development of more useful reliable techniques for evaluation of critical performance parameters for materials than those currently in existence. Often the evaluation methods are not well defined or are inefficient and/or expensive to conduct. The objective of the present investigation is directed toward development of standard test methodologies which will meet the needs of the dental industry/profession in development and control of alloy and ceramic products, both as starting materials and in processing through to final systems as dental prostheses.

### A. Alloy Castability

A technique for determining a castability value, $C_v$, for a dental alloy has been described in previous reports [2]. In essence, $C_v$ is the percentage of cast alloy segments which comprise a rectangular grid (fig. 27). Castability in this case is considered as the ability of an alloy to fill a mold under specific conditions including mold and alloy temperature.

The evaluation technique has been applied to a number of dental alloys to determine the ability to distinguish between alloys under a set of prescribed conditions (Table 31). Results of this examination are shown in fig. 28 and clearly indicate that significant differences can be shown to exist between many of the alloys, i.e. the method can distinguish between the castability values of different alloys. It

Pattern

| | |
|---|---|
| Test Portion: | 1 mm opening (No. 18) polyester sieve cloth, 10 x 10 sq. |
| Runner Bars: | 10 gage round wax |
| Sprue: | 6 gage round |
| Sprue Length: | 10 mm |

Mold

| | |
|---|---|
| Ring: | Whip-Mix 1.5" x 2" |
| Liner: | 1 layer, damp asbestos |
| Mixing Conditions: | Full strength liquid ($H_2O$ - Ceramigold II) investment manufacturers' recommended L/P ratios vacuum mix, 400 rpm, for 1 min, vibrate 30 sec. |
| Setting Conditions: | Hygroscopic technique, 100°F water bath, 45 min. |
| Burnout: | 1 hour to alloy manufacturers' recommended, temperature, 1 hour heat soak |

Casting

| | |
|---|---|
| Weight of Alloy: | Base metal 11.5 - 13 g, Olympia, Cameo and W-1, 12.4 g (8 DWT) Triumph 10.9 g, Jelenko "O" 10.1 g (6.5 DWT) |
| Machine: | Howmedica Electromatic, induction melting |
| Temperature: | Alloy manufacturers' recommended temperature |
| Melt Soak Time: | Alloy manufacturers' recommended time or 10 sec. if not specified |
| Speed: | 400 rpm at maximum acceleration |
| Crucible: | Heat soaked at mold temperature for 30 min. |
| Pattern Orientation: | Vertical |

Table 31, Standard Evaluation Procedure

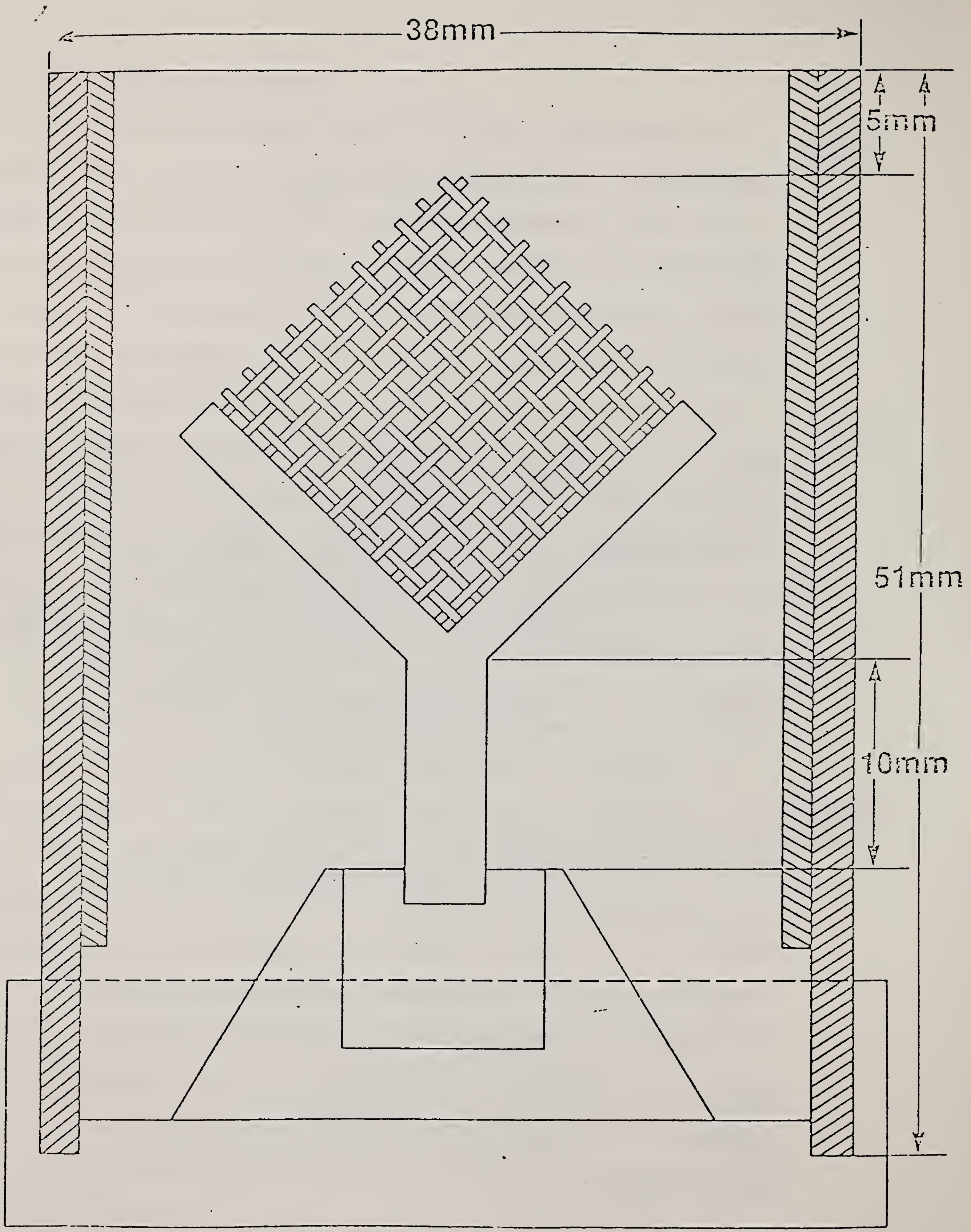


Figure 27

CASTABILITY

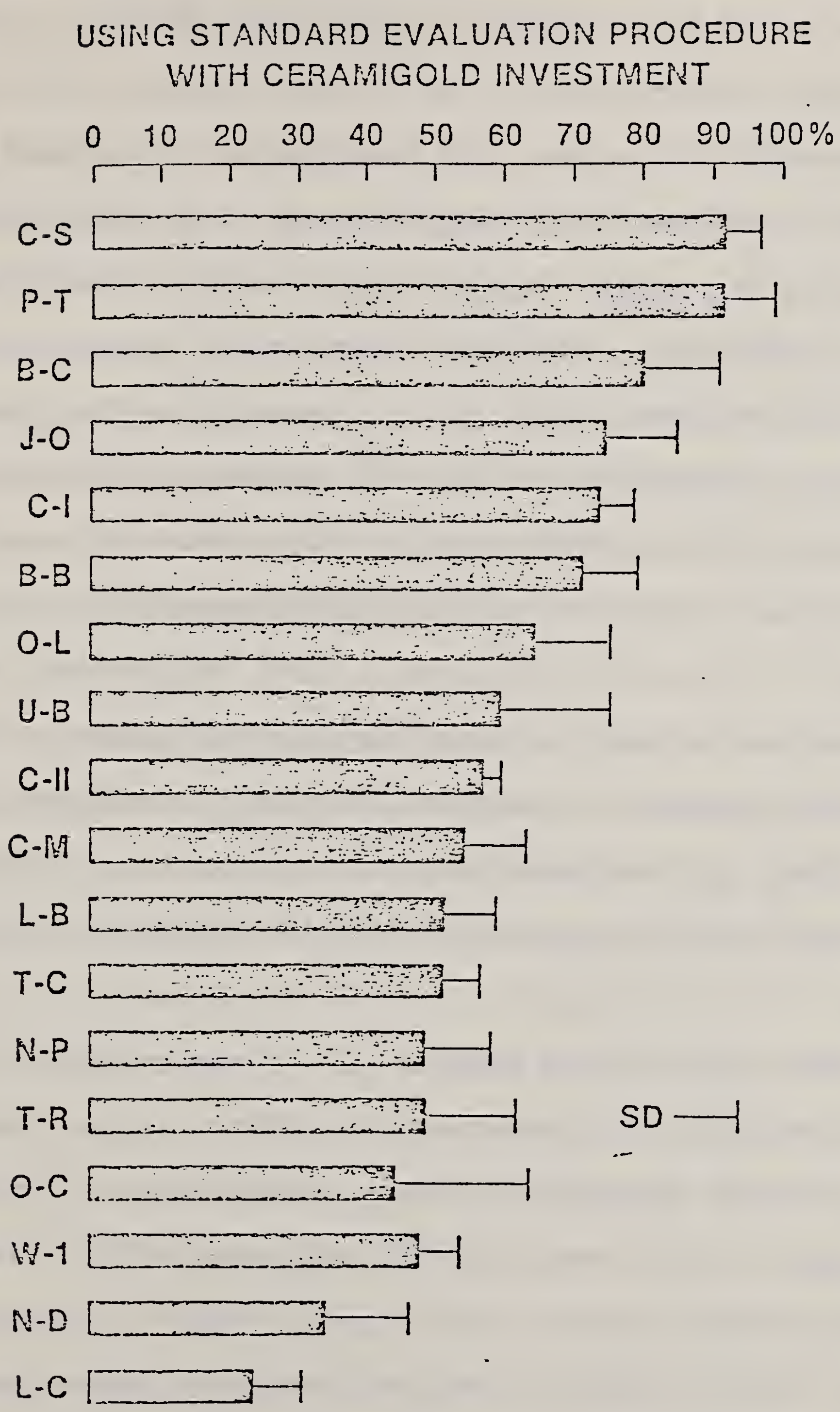


Figure 28.

should be noted, however, that the results do not define what an acceptable castability value must be; it defines the value which should be expected for a consistently produced alloy or for an alloy used under controlled conditions in a dental laboratory. The investigation was extended to examine effects of different mold temperatures and alloy temperatures on castability (figs 29 and 30). This has been reported (see Abstracts 1982, Use of a Castability...etc.) and a manuscript is in review for publication. In total, the results show the dependence of the castability value $C_v$ on temperatures and that the standard deviation (SD) is itself a function of the castability value, being small under conditions which render $C_v$ near the extremes of its possible range for each alloy. This variation of SD could be interpreted as being indicative of the ability to consistently obtain good castings under a given set of conditions. Because SD itself appears to be somewhat an indicator of the consistency with which castings may be repeatedly made to the same level of quality it can be a useful tool in conjunction with $C_v$ for optimizing casting conditions.

To determine, by regression analysis, the optimum conditions for castability of an alloy, it is necessary to have SD as a known function of $C_v$. An alternative approach is to find a transformation, $\overline{C_v}$ , of $C_v$ which will render the transform of SD, $\overline{SD}$, independent of $\overline{C_v}$. This matter has been pursued with Mr. Harold Argentar (formerly with the American Dental Association Health Research Foundation, then a Guest Worker with NBS, and currently an independent consultant) who found that standard transformations are not adequate and the transform

$$\overline{X} = \ell n \frac{2/3-\sqrt{C_v}}{2/3-\sqrt{1-C_v}}$$

appears to work well. An abstract has been prepared for presentation of this at the AADR, 1983. Assuming separation of variables, one may write 1) $C_v = f(T_A)g(T_m)h(C_i)$ where $T_A = (T_{alloy} - T_{melting})$, $T_m$ = mold temperature and $C_i$ are ith concentrations of various alloy elements. Similarly, 2) $\overline{C_v} = F(T_A)G(T_m)H(C_i)$ where F, G and H are independent functions. Functions will be assumed for F, G and H, and regression analysis conducted for representation of the overall effects of the three variables, $T_A$, $T_m$, and $C_i$. A more complete discussion is planned for presentation at the AADR, 1983.

If one assumes that the major effect of repeated castings of dental alloys is change in $C_i$, then effects on $C_v$ of repeated castings should be calculable from the functional representation of $C_v$ (or $\overline{C_v}$) and using before and after chemical analysis of various elements in an alloy. A program has been devised for leading to determination of $C_v$ $(C_i)$ via multivariant analysis of $C_v$ for alloys of several compositions. This will require additional determinations of $C_v$ to cover effects of Si, Ga, Be, Bo, Mm, Sn, etc. Casting studies of additional alloys are in progress and results for Ceramalloy II will be presented. If one assumes $f = a+bT_A+cT_{A_g}^{\;2}$, $g = d+eT_m$; and for h = constant requires that $C_v = 0$ at $T_A = 0$, then an expression for $C_v$ is given by

$$C_v = A\ T_A + B\ T_A^2 + C\ T_A T_m + D\ T_A^2 T_m\ .$$

Other functions, of course, can be attempted for obtaining the best fits to the data.

## B. Porcelain-Alloy Stress Compatibility

Failure of porcelain fused-to-metal restorations is often attributed

# CASTABILITY

## USING STANDARD EVALUATION PROCEDURE WITH RECOMMENDED CASTING TEMPERATURE AND INVESTMENT

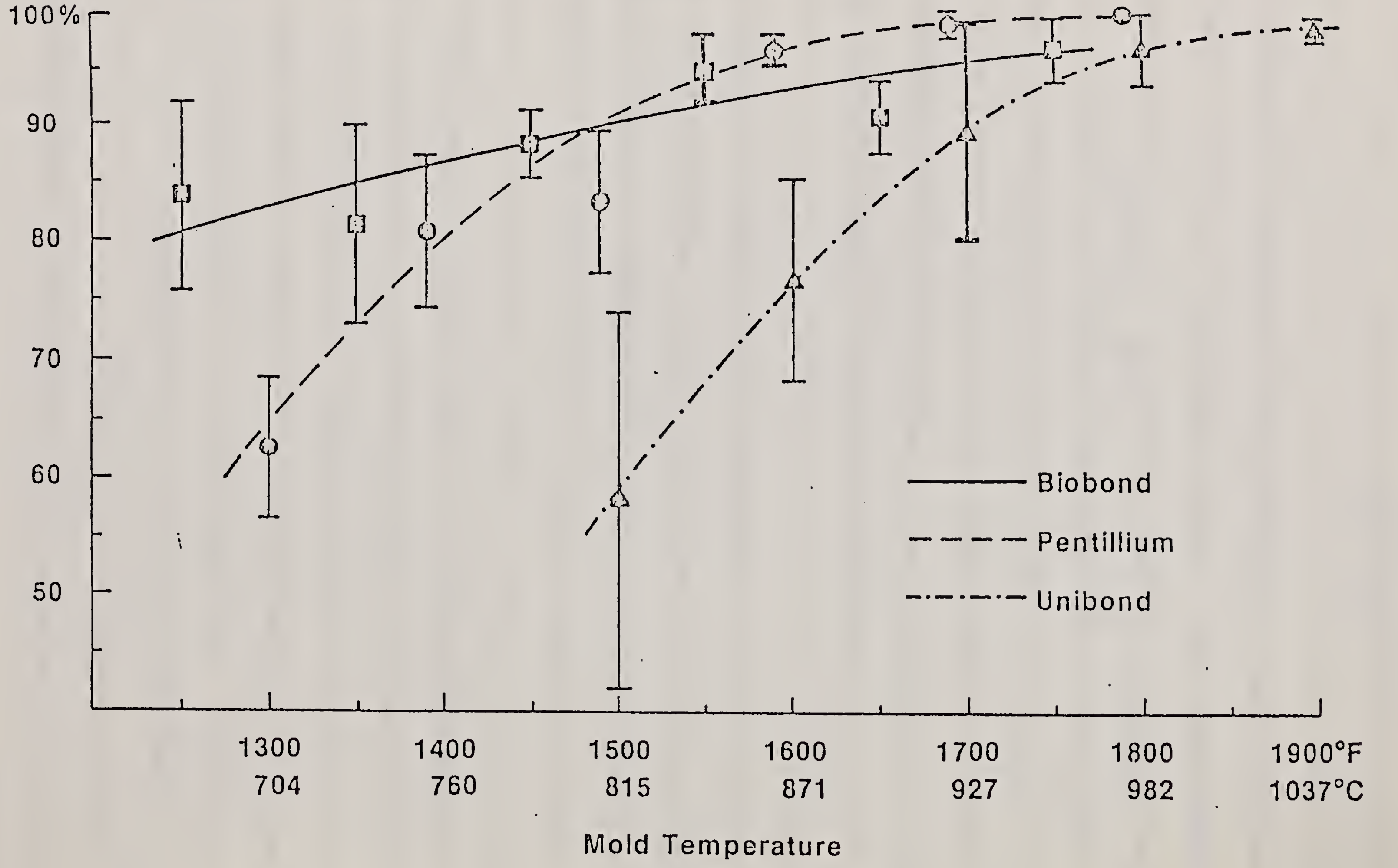


Figure 29.

## CASTABILITY

### USING STANDARD EVALUATION PROCEDURE WITH RECOMMENDED MOLD TEMPERATURE AND INVESTMENT

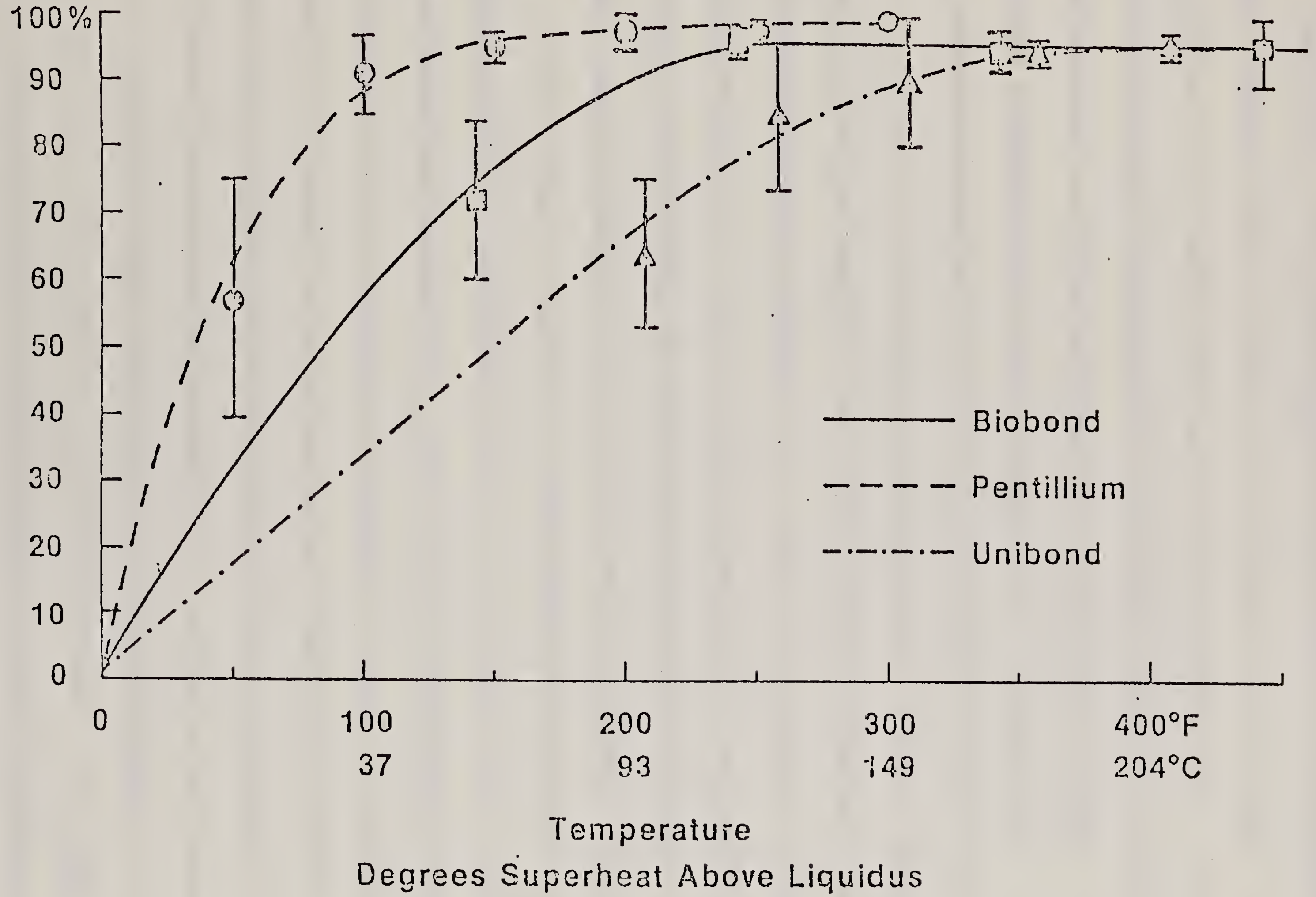


Figure 30.

to residual stress in porcelain following the porcelain firing cycle. This stress has its origin in the differences in thermal expansion which exist between porcelain and alloy throughout the firing temperature range. However, other properties also affect the final level of stress retention. These include thermo-viscoelastic properties (primarily of the porcelain), thermal conductivity and temperature dependent elastic moduli. Geometric variations in restorations are also a contributing factor. The objective of this phase of study was to develop a technique which can be used to experimentally confirm or indicate stress compatibility and to back it with a firm theoretical analysis.

The experimental portion of this work utilizes the change in gap of a porcelain veneered split metal ring to reflect the strain generated by residual stresses. Theoretical analysis via the finite element method is to be used to verify strain predictions by comparison with experimental gap change calculations and to then calculate residual stresses. The computer simulation requires the use of a number of experimentally determined input properties as previously mentioned. Progress on this project has proceeded in several items, 1) theoretical considerations of the dependence of stress on mechanical properties, 2) calculation of the extent to which experimental measurements may be affected by diffusion bonding of porcelain and alloy (and also various porcelain layers), 3) experimental determination of the temperature dependence of elastic moduli, 4) construction of final FEM's (finite element models).

Item 1:

Theoretical studies of the dependence of stress and strain (gap changes) on mechanical properties showed that neither stress nor strain were affected significantly (less than one percent) by choice of Poisson's ratio for porcelain or alloy. Stress was greatly affected by the values for elastic moduli which were chosen but strain was not affected to a significant degree. A manuscript for publication has been prepared and has cleared NBS review.

Item 2:

The effects of diffusion bonding between different layers of porcelain and porcelain and alloy have been investigated theoretically. Calculations were extended to investigate effects of opaque layers having various thicknesses and thermal expansion properties and also the affects of diffusion bonding on thin layers of glaze. A manuscript has been accepted for publication in the Journal of Dental Research and results are summarized as follows:

1. The strain measured on multimaterial layered split rings or flat strips is unaffected by changes in thermal expansion when the thickness of porcelain ($t_1$) + diffusion zone ($t_2$)/alloy thickness ($t_3$), $(t_1 + t_2)/t_3 \gtrsim 0.8$ m/0.5 mm (note that 0.025 mm is the experimental limit of detection.)
2. Total strain decreases as $t_{porcelain}/t_{alloy}$ increases above $t_1/t_3 \approx 1$.
3. Total strain is maximized with noble alloys for $t_1/t_3 \approx 1$. This would also indicate that distortion of clinical porcelain-fused-to-metal fixed partial denture restorations is similarly reduced by either higher or lower ratios, $t_1/t_3$.
4. For nonprecious alloys, total strain is always lower for $t_1/t_3 > 1$. A ratio $t_1/t_3 \sim 0.8$ mm/0.5 mm significantly reduces total strain. This indicates that PFM restorations might also be distorted by the condition $t_1/t_3 > 1$.

5. For low porcelain/alloy ratios, $t_1/t_3 \lesssim .2/.5$ detectable interfacially induced strain can be produced from interfacial layers as thin as 1 to 6 $\mu$m if the thermal expansion of the interface is radically changed (by a factor of two for example.)
6. For porcelain layers much thinner than alloy, $t_1/t_3 \lesssim 0.2/0.5$, nonprecious alloys generate lower interfacially induced strain than gold alloys.
7. For noble alloy-porcelain interfaces less than 8 $\mu$m thick, interfacially induced strain is always lowest for equal thicknesses of porcelain and alloy.
8. By proper choice of porcelain/alloy ratios, experimental information on the properties of different layers might be obtained. For example, for noble alloys, choosing $t_1/t_3 \approx 0.5/0.5 = 1$, total strain is maximized and interfacial effects are minimized. For low porcelain/alloy thickness ratios, interfacial effects become detectable. An example of this would be the application of a glaze to a body porcelain. Diffusion could change the thermal expansion coefficient of the glaze relative to that obtained from bulk measurements of the glaze.
9. Although proper choice of $t_1/t_3$ may minimize interfacially induced strain effects and strain correlations between theory and experiment obtained via use of bulk properties, stress at the interface might be significantly altered by the changes in the interface. Knowledge of the interfacial stresses would be important in the overall determination of compatibility.

10. Changes in elastic moduli, $E_2$, of interfacial zones are expected to produce insignificant strain effects over the range $0.3 \leq E_2/E_3 \leq 3.3$ (here $E_3$ is the modulus of the alloy).

Item 3

Because the amount of stress retention (or relaxation) which can take place at high temperatures will depend on the elastic constants at those temperatures it is of value to know the temperature dependence of the elastic moduli. A sonic technique with the necessary apparatus has been borrowed from the Fracture and Deformation Group of NBS for this purpose. Calculations have shown that specimens ~ 5 cm x 1 cm x 0.2 cm should provide the best response for both alloy and porcelain for measuring shear and longitudinal resonance frequencies. Specimens have been prepared and experiments are just beginning. Preliminary results for Ceramco and Vita porcelains have been obtained which show the Young's modulus at 68.2 GPa for Vita VMK68 porcelain and 69.2 GPa for Ceramco porcelain. Increasing temperatures result in a decreasing modulus for each. An abstract has been submitted on this for presentation at the AADR meeting in 1983.

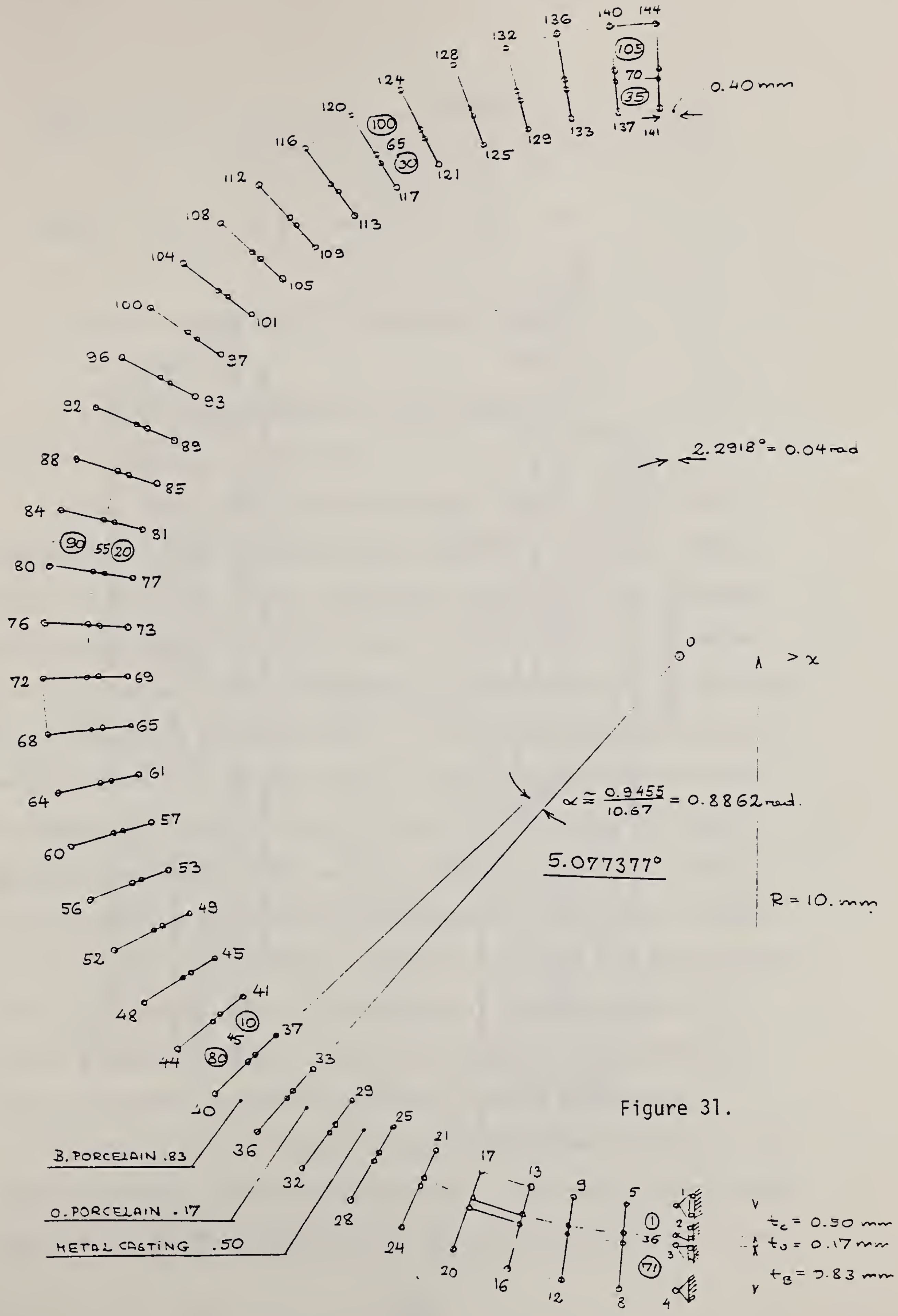
Item 4

A number of finite element models have been constructed for making preliminary studies, for example: on gap change without incorporating temperature gradients or stress relaxation and for stress distributions under those conditions or on the effects of elastic properties on stress and strain. None of the programs devised thus far have been able to carry out a complete analysis with all variables accounted for.

One of the prime difficulties lay in finding (or developing) a computer program which allowed for temperature dependent stress relaxation (thermo-visco-elastic behavior) while at the same time calculating time dependent temperature gradients. A major obstacle was the lack of high symmetry and the need to maintain aspect ratios for each element; the thinness of the ring resulted in an unwieldy number of elements (Fig. 31). These problems were overcome by noting that the small gap, $\sim$ 1 mm, in a circumference of $\sim$ 32 mm resulted in nearly axial symmetry. This was utilized for calculation of radial temperature gradients for most of the ring. Detailed element calculations were then carried out on small sections which were required to meet temperature and equilibrium conditions for the rest of the ring (for which temperature profiles had been obtained from the axial symmetry calculations). A trial run has been made with the new model and program and the program runs to completion. The next step will be to input experimentally determined properties for a rough comparison of theoretical and experimental gap changes. The final steps will involve using experimentally determined boundary cooling rates for fine tuning of the system for coincidence of calculated and experimental gap changes.

### C. Porcelain-to-Metal Bond Strength.

A simple, bending-beam-composite (BBC) was proposed late in 1981 for evaluation of the porcelain-to-metal bond strength (Fig. 32) and two papers were presented on this at the 1982 meeting of the AADR. With the specimen shown, up to four fractures can be obtained, there will be either porcelain-metal bond strength (PMBS) fractures or porcelain rupture strength fractures (PRS). According to simple beam theory, the failure stress $\sigma_{\text{PMBS or PRS}}$ is given by

136
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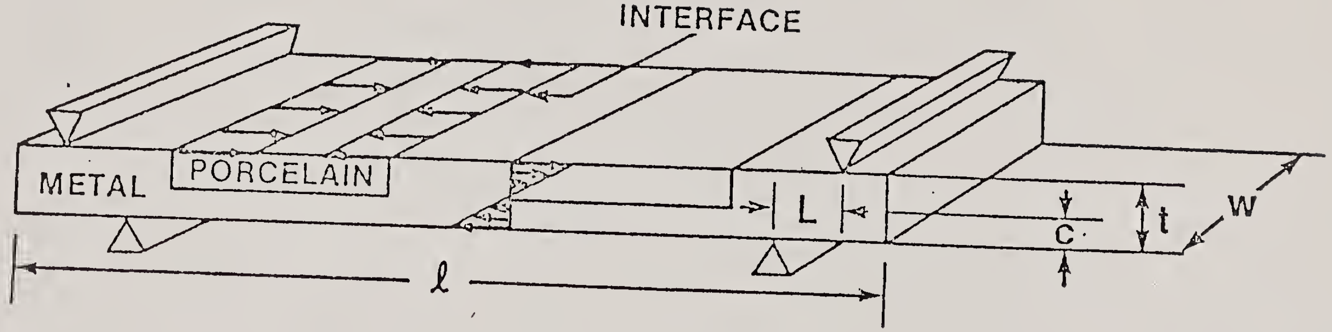
81
85
89
93
97
101
105
109
113
117
121
125
129
133
137
141
105
70
35
100
65
30
90
55
20
10
45
80
1
36
71
0
0.40 mm
2.2918° = 0.04 rad
$\alpha \cong \frac{0.9455}{10.67} = 0.8862$ rad.
5.077377°
R = 10. mm
y
> x
B. PORCELAIN .83
O. PORCELAIN .17
METAL CASTING .50
$t_c = 0.50$ mm
$t_o = 0.17$ mm
$t_B = 0.83$ mm

Figure 31.



Bending Beam Composite specimen comprised of alloy beam and porcelain sections. Application of a force, F/2 to the knife edges produces a bending moment M, which is constant between the inner knife edges. This produces a constant stress along the surface of porcelain sections as is indicated by the vectors in the left section. The right section shows the stress gradient within porcelain, with the maximum stress at the surface.

Figure 32

$$\sigma_{\text{PMBS or PRS}} = \frac{6F\ell(t-\bar{y})}{w\left[b^3+nc^3+12\left(b[(c+b/2)-\bar{y}]^2+nc[c/2-\bar{y}]^2\right)\right]}$$

where $\bar{y} = 1/2\left(\dfrac{t^2+c^2(n-1)}{t+c(n-1)}\right)$ and

F = 2x the applied force for the bending moments

L = the moment arm

n = Modulus of Metal/Modulus of Porcelain

Terms are according to figure 32.

The beam model stress calculations were checked by the finite element method (FEM) and showed smooth transition in surface stress across the interface. These calculations also showed some curvature in the stress field in porcelain away from the interface at a few mm from the interface. FEM calculations also confirmed that for the dimensions of specimens for which $c/t \sim .3 - .5$ mm, the stress is virtually independent of c/t (fig. 33). For $n > 1$ the stress transition across the interface is not only smooth, but the surface stress difference between the maximum in metal and the minimum in porcelain is almost equally divided by two at the interface and the transition is gradual for several mm in the porcelain. Hence, for example, the 14% difference (fig. 33) translates into a 7% difference at the interface and the gradual nature of the stress transition results in an uncertainty of only a few percent in PMBS calculations by simple beam theory.

The effects of first fracture cracks on subsequent failures is the subject of recent, ongoing FEM calculations. The results indicate that under totally elastic conditions, St. Venant's principle is valid and

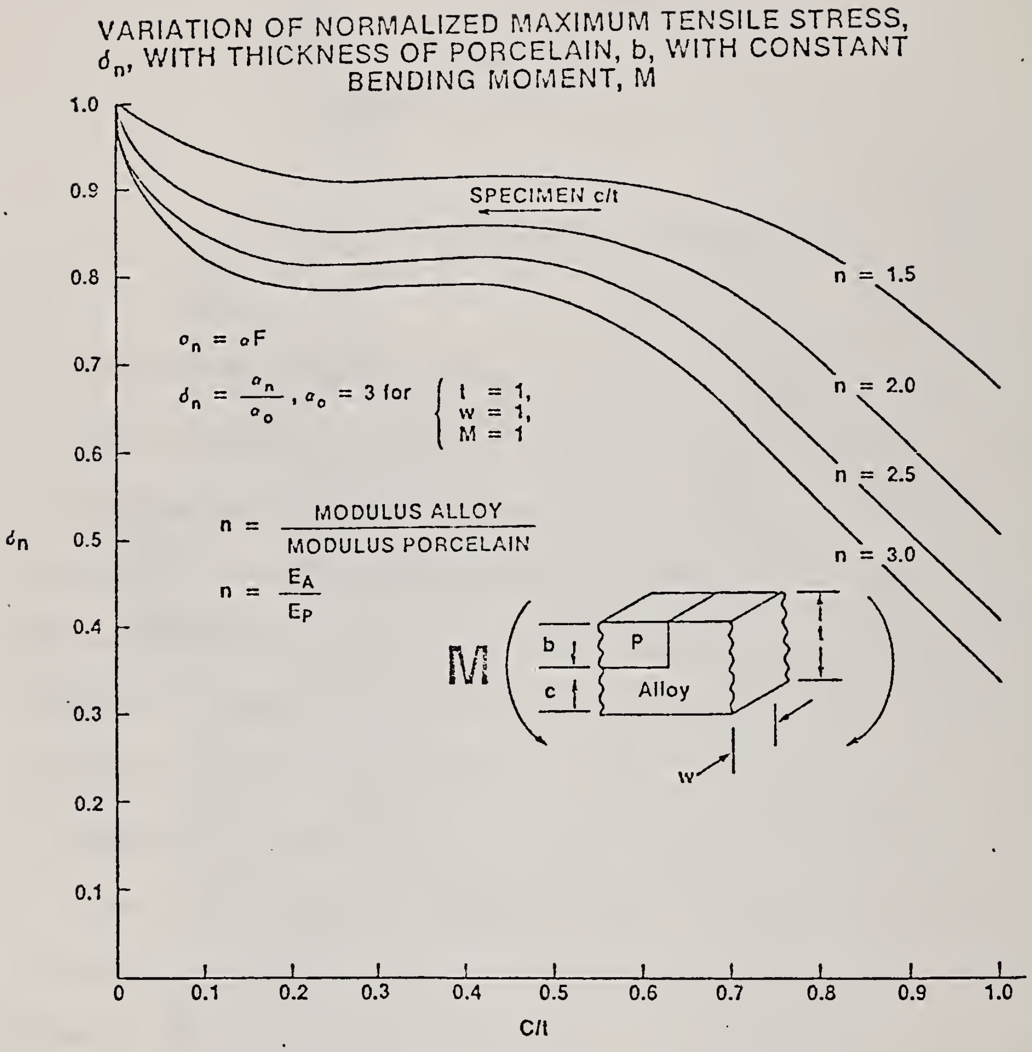


Figure 33. $\sigma_f$ (PMBS or PFS) as a function of load, F, applied to fixture (which provides load F/2 at each knife edge (fig. 32) and specimen properties and goemetry. All symbols have been defined in text.

for specimen dimensions which have approximately 1 cm slabs of porcelain the fracture at one interface does not influence fracture stresses at other interfaces. The key point, however, is that the conditions must be elastic. Experimentally, it has been observed that stress relaxation in the metal will cause fractures in other interfaces at lower applied loads, F. This is interpreted as being due to higher stress being borne by the porcelain than would be calculated by elastic theory.

The new test method has been received well by industry and three major dental companies* have cooperated in further investigations by supplying "visitor" workers for one week each at NBS. The results of studies on specimens of these materials have shown the test method capable of distinguishing (at the .05 level), between experimental systems known to produce weaker bonding and those producing stronger bonding. Experimental fractures near the interfaces also showed the types of curvature predicted from the FEM. Two abstracts on this work were submitted for the 1983 meeting of the AADR.

### D. Fit and Soldering of Dental Alloy Castings

No work was done on this phase of the project due to concentration of efforts on the preceeding sections.

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* Dentsply International, York PA
Williams Gold and Refining Co., Buffalo, NY
Howmedica, Inc., Dental Div., Chicago, IL

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## Invited Talks (1982)

Initiator-Accelerator Systems for Dental Application. G. M. Brauer, American Cehmical Society Symposium, Las Vegas, NV

A Dental and Medical Materials Program at NBS. J. M. Cassel, Johns Hopkins University, Baltimore, MD

Wear Mechanisms in Dental Composites. W. Wu, Symposium on Materials, American Association of Dental Schools, New Orleans, LA.

A Small Angle X-ray Study of Particulate Reinforced Composites. W. Wu, International Union of Pure and Applied Chemistry, Macromolecules Session, Amherst, MA

Castability and Fit of Nonprecious Alloys. J. A. Tesk, Eastern Maryland Dental Society, Ocean City, MD

Recent Developments in Metals as Dental Bio/Alloys. J. A. Tesk, R. W. Hinman[1], R. M. Waterstrat[2] and W. deRijk[2], Symposium on Recent Developments in Biological Alloys, AIME, Dallas, TX

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ABSTRACTS IADR/AADR MEETING, MARCH 82, NEW ORLEANS (ON MICROFILM):

A Quantitative/Expedient Porcelain-to-Metal Bond Test, Part I: Theoretical Basis. J. A. Tesk, G.E.O.Widera[1], R. W. Hinman[2], W. deRijk[3].

Cements Containing Vanillate Esters, EBA and Zinc Oxide. G. M. Brauer and J. W. Stansbury.

Use of a Castability Test for Optimizing Mold and Casting Temperature. R. W. Hinman, J. A. Tesk, R. P. Whitlock[4], E. E. Parry[4], and J. S. Durkowski[4],

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

Subsurface Wear Defects Analysis of Both *In Vivo* and *In Vitro* Dental Restorative Composites. W. Wu, E. E. Toth and J. P. Moffa[5].

Influence of Chemical Softening on Wear of Three Types of Dental Composites. J. E. McKinney and W. Wu.

A Quantitative/Expedient Porcelain-To-Metal Bond Test, Part II. Preliminary Results. W. G. deRijk, J. A. Tesk, R. W. Himnan, E. E. Parry, M. Conner[6], G. E. O. Widera.

Effect of Thermal Parameters on Compatibility in Porcelain Veneered Split Metal Rings. G. E. O. Widera, N. Munir[7], J. A. Tesk, R. W. Hinman.

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## ABSTRACTS SUBMITTED FOR 1983 AADR MEETING

Castability of Dental Alloys, Repeated Casting, Mold and Alloy Temeprature Effect. S. Hirano[1], J. A. Tesk, and R. W. Hinman[2].

Dental Cements Containing Hexyl Syringates. G. M. Brauer and J. W. Stansbury.

Divanillates and Polymerizable Vanillates as Ingredients of Dental Cements. J. W. Stansbury, G. M. Brauer and J. M. Antonucci.

Effect of Degree of Cure on Hardness and Wear of Three Commercial Dental Composites. J. E. McKinney and W. Wu.

Effect of Elastic Modulus on Stresses in Ceramo-metal Systems. J. A. Tesk, R. W. Hinman, W. deRijk[3], H. R. Kase[4].

Elastic Constants of Two Dental Porcelains, H. R. Käse, E. Case[5], and J. A. Tesk.

Factors Controlling the Degree of Polymerization of Dental Resins. W. Wu.

Formulation and Evaluation of Fluorine-Containing Composite Resins. J. M. Antonucci, S. Venz[6], G. M. Brauer, J. W. Stansbury and D. J. Dudderar.

Functional Representation of a Castability Value, $C_v$, for Dental Alloys. R. W. Hinman, J. A. Tesk, H. Argentar[7] and S. Hirano[1].

Microleakage and Water Sorption of Hydrophilic and Hydrophobic Dental Composites. S. Venz, N. W. Rupp[3] and J. M. Antonucci.

Porcelain to Metal Bond Strength Measurements as Determined by the Four Point Bending of a Composite Beam. W. G. deRijk[3], J. A. Tesk, M. Connor[8] and K. A. Jennings[8].

Stress Analysis of Bond Test Specimen. G. E. O. Widera[9], J. A. Tesk, W. J. deRijk, and R. W. Hinman.

## ADDITIONAL ABSTRACTS (FY83)

Acrylic Resin Compatible Adhesive Cements. G. M. Brauer and J. W. Stansbury, Table Clinic, Maryland State Dental Association Annual Meeting, Baltimore, MD, Oct. 7-10, 1982

A SANS Investigation Into the Plastic Deformation Mechanisms of Polyethylene. W. Wu. American Physical Society, March 1983.

Beryllium, The Need for and Uses in Dental Alloys. J. A. Tesk, Invited for Symposium on Non Precious Alloys, American Association of Dental Schools, March 1983.

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## PAPERS PUBLISHED (FY82)

1. Hardening Shrinkage of Hydroscopic Expansion of Composite Resins. R. L. Bowen, J. Rapson and G. Dickson. J. Dent. Res. 61(5), 654-60 (1982).

2. Relationship Between Subsurface Damage and Wear of Dental Restorative Composites. J. E. McKinney and W. Wu. J. Dent. Res. 61(9), 1083-88 (1982).

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4. Influence of Filling Material and Silanization Method on Strength and Marginal Adaptation of Experimental Composites. K. Dermann, G. M. Brauer, and N. W. Rupp. Deutsch Zahnarztl. A. 37, 160-163 (1982).

## MANUSCRIPTS IN REVIEW OR ACCEPTED FOR PUBLICATION

1. Small Angle Neutron Scattering of Partially Segregated Polymer Blends. W. Wu, accepted for publication in Polymer.

2. Application of Small Angle X-ray Technique in Damaged Particulate Reinforced Composites - A Theoretical Treatment, W. Wu, accepted for publication in Polymer.

3. Effects of Porcelain/Alloy Interfacial Diffusion Zones on Thermomechanical Strain. J. A. Tesk, R. W. Hinman, G. E. O. Widera, A. D. Holmes and J. M. Cassel. Accepted for publication in J. Dental Research.

4. Physical Metallurgy of Dental Casting Alloys, Parts C. Cr-Co-Mo System, D. Ni-Cr System, E. Fe and Austenitic Stainless Steel, and F. Titanium Alloys. J. A. Tesk and R. M. Waterstrat. Accepted for publication in Encyclopedia of Materials Science and Engineering.

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6. Subsurface Damage Layer of In Vivo Worn Dental Composite Restorations. W. Wu, E. E. Toth, J. F. Moffa, J. A. Ellison, to be submitted to J. Dent. Res.

7. Post Curing of Dental Restorative Resins, W. Wu and B. M. Fanconi, to be submitted to Polymer Science & Engineering.

8. Development of High Strength Acrylic Resin-Composite Adhesive Cements G. M. Brauer, J. W. Stansbury, accepted for publication in J. Dent. Res.

9. Influence of Chemicals In vitro Wear of Dental Restorative Materials. W. Wu and J. E. McKinney, accepted for publication in J. Dent. Res.

10. Wear Mechanisms of Dental Composite Restorations. W. Wu. Submitted to Polymer.

11. Solvent Effects on Bonding Organosilane to Silica Surfaces. T. M. Chen and G. M. Brauer. Submitted to J. Dent. Res.

12. Effect of Hygrophilic Diluents on the Properties of Cured Composites. K. Dermann, N. W. Rupp and G. M. Brauer. Accepted for publication in J. Dent. Res.

13. Intraoral Secondary Radiation Dose from Neutron Activated Dental Materials. J. A. Tesk, R. P. Whitlock and A. D. Holmes. To be submitted to Medical Physics.

14. Theoretical/Experimental Studies of Stress Compatibility in Porcelain Veneered Split Metal Rings. G. E. O. Widera, J. A. Tesk, R. W. Hinman, and N. Munir. To be submitted to J. Biomedical Materials Research.

15. Fit of Multiple Unit Fixed Partial Denture Castings. R. W. Hinman, J. A. Tesk, E. E. Parry and G. T. Eden. To be submitted to Journal of Prosthetic Dentistry.

16. A Practical Method for Evaluating the Castability of Dental Alloys. R. W. Hinman, J. A. Tesk, R. P. Whitlock, E. E. Parry and J. J. Durkowski to be submitted to J. Dental Research.

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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)*

Dental cements based on esters of vanillic acid display excellent long term solubility characteristics. Modification of formulations yield uniquely high strength properties and the potential for high strength intermediate restorative resins. Polmeric formulations designed to reduce curing shrinkage, residual unsaturation and hydrophilicity in composites have been developed. A high molecular weight polythiol, pentaerythritol tetra(3-mercaptopropionate), contributes toward this goal and improves color and color stability. Deterioration of composite restorative materials exposed to solvents simulating food debris is maximal in 75% ethanol-water solutions as judged by silver stain examination, changes in surface hardness and wear loss. The resin matrix as cured at 37°C has a low degree of polymerization (DP) and is susceptible to softening by penetrating molecules. Infrared spectroscopy revealed that the DP in a composite is more sensitive to monomer composition than to initiator type or concentration. The rate of solvent-induced softening of composites depends on the cure temperature. A bending beam porcelain-metal specimen was designed. Initial four point bending results obtained in collaboration with dental manufacturers indicate the potential for a simple, reproducible, informative test. Alloy castability values generated in a new test method are strongly dependent on mold and alloy temperatures. Data variance can be used to optimize casting conditions.

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

Castability; cements; compatibility; composites; polymerization; porcelain/alloy; and wear resistance.

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